VOLUME LX NUMBER 4

THE ASTROPHYSICAL JOURNAL

AN INTERNATIONAL REVIEW OF SPECTROSCOPY AND ASTRONOMICAL PHYSICS

EDITED BY

GEORGE E. HALE
Mount Wilson Observatory of the Carnegie Institution of Washington

EDWIN B. FROST
Yerkes Observatory of the University of Chicago

HENRY G. GALE
Ryerson Physical Laboratory of the University of Chicago

NOVEMBER 1924

THE UNIVERSITY OF CHICAGO PRESS
CHICAGO, ILLINOIS, U.S.A.

THE CAMBRIDGE UNIVERSITY PRESS, London
THE MARUZEN-KABUSHIKI-KAISHA, Tokyo, Osaka, Kyoto, Fukuoka, Sendai
THE MISSION BOOK COMPANY, Shanghai

November 1924 Vol. LX, No. 4

THE ASTROPHYSICAL JOURNAL

AN INTERNATIONAL REVIEW OF SPECTROSCOPY AND ASTRONOMICAL PHYSICS

The Astrophysical Journal is published by the University of Chicago at the University of Chicago Press, 5750 Ellis Avenue, Chicago, Illinois, during each month except February and August. ¶The subscription price is $6.00 a year; the price of single copies is 75 cents. Orders for service of less than a half-year will be charged at the single-copy rate. ¶Postage is prepaid by the publishers on all orders from the United States, Mexico, Cuba, Porto Rico, Panama Canal Zone, Republic of Panama, Dominican Republic, El Salvador, Argentina, Bolivia, Brazil, Colombia, Costa Rica, Ecuador, Guatemala, Honduras, Nicaragua, Peru, Uruguay, Hawaiian Islands, Philippine Islands, Guam, Samoan Islands, and Spain. ¶Postage is charged extra as follows: for Canada, 30 cents on annual subscriptions (total $6.30); on single copies, 3 cents (total 78 cents); for all other countries in the Postal Union, 50 cents on annual subscriptions (total $6.50), on single copies 5 cents (total 80 cents). ¶Patrons are requested to make all remittances payable to The University of Chicago Press in postal or express money orders or bank drafts.

The following are authorized to quote the prices indicated:

For the British Empire: The Cambridge University Press, Fetter Lane, London, E.C. 4. Yearly subscriptions, including postage, £1 16*s*. each; single copies, including postage, 4*s*. 6*d*. each.

For Japan and Korea: The Maruzen-Kabushiki-Kaisha, 11 to 16 Nihonbashi Tori Sanchome, Tokyo, Japan. Yearly subscriptions, including postage, Yen 13.65 each; single copies, including postage, Yen 1.68 each.

For China: The Mission Book Company, 13 North Szechuen Road, Shanghai. Yearly subscriptions, $6.00; single copies, 75 cents, or their equivalents in Chinese money. Postage extra, on yearly subscriptions 50 cents, on single copies 5 cents.

Claims for missing numbers should be made within the month following the regular month of publication. The publishers expect to supply missing numbers free only when losses have been sustained in transit, and when the reserve stock will permit.

Business Correspondence should be addressed to The University of Chicago Press, Chicago, Illinois.

Communications for the editors and manuscripts should be addressed to the Editors of THE ASTROPHYSICAL JOURNAL, Ryerson Laboratory, University of Chicago, Chicago, Illinois.

The cable address is "University, Chicago."

The articles in this Journal are indexed in the *International Index to Periodicals*, New York, N.Y.

Entered as second-class matter, January 17, 1895, at the Post-office at Chicago, Ill., under the Act of March 3, 1879.

Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized on July 15, 1918.

PRINTED IN THE U.S.A.

THE

ASTROPHYSICAL JOURNAL

AN INTERNATIONAL REVIEW OF SPECTROSCOPY AND ASTRONOMICAL PHYSICS

VOLUME LX NOVEMBER 1924 NUMBER 4

PHOTO-ELECTRIC PROPERTIES OF THIN FILMS OF ALKALI METALS

By HERBERT E. IVES

ABSTRACT

The thin films of alkali metals which deposit spontaneously on clean metal surfaces in highly exhausted inclosures are studied. The alkali metals, sodium, potassium, rubidium, and caesium, in the thin film form all exhibit, to a striking degree, the selective photo-electric effect first discovered in sodium-potassium alloy. Experiments on varying the thickness of the deposited film show that the selective effect only occurs at a certain stage of the film's development; for very thin films the selective effect is absent, and it disappears again for thick layers of the pure alkali metal. The wave-length maxima of emission previously ascribed to the selective effect in the pure alkali metals on the basis of observations with rough or colloidal surfaces are absent in these thin films.

INTRODUCTION

Elster and Geitel[1] observed that the alkali metals, when placed in well-evacuated inclosures, quickly coat all parts of the inclosures, by the diffusion of their vapors, with a photo-sensitive layer. They made some experiments on the readiness with which such spontaneously deposited films accumulated on various materials and verified the proportionality between illumination and photo-electric current.

The present work grew out of the observation that a tungsten filament at the center of a bulb, whose walls were coated with potassium, was photo-electrically sensitive. Heating the filament to

[1] Geitel, *Annalen der Physik*, **67**, 420, 1922.

incandescence and thereby driving all the potassium off destroyed this sensitiveness, but within a few seconds after the heating current was turned off the filament was again sensitive, regaining practically its entire sensitiveness within a few minutes. The experiments which are here described have to do with the properties of these spontaneously formed films in the cases of the four alkali metals, sodium, potassium, rubidium, and caesium, as deposited on plane, highly polished sheets of metal, which in the majority of the experiments were platinum. Observations have been made with the incident light polarized in both principal directions, and the films have been studied in varying thicknesses as obtained either by arranging that the deposition shall take place slowly or by evaporating the alkali metal off on to the artificially cooled walls of the inclosing cell.

TYPES OF PHOTO-ELECTRIC CELL USED

A considerable number of special cells were constructed for this study, with gradual modifications of details. One of the final forms, on which the majority of observations were made, is illustrated in Figure 1, and may be described as characteristic of all. It consists of a cylindrical bulb with a relatively long neck of smaller diameter. A stem entering through the long neck carries a flat polished piece of platinum, and, also, a short distance behind the platinum sheet, a tungsten filament which is arranged so that it may be caused to glow by the passage of a current. In contact with the walls of the cell is a nickel cylinder with a rectangular opening extending through 180° in front of the platinum plate and with a large irregular opening behind. Extending outward from the neck is a side tube filled with charcoal, for immersion in liquid air. The cell, which is of pyrex glass, is exhausted to a high vacuum by a mercury diffusion pump working through a liquid air trap, the whole cell being baked to 400° C. during the process of exhaustion, which takes several hours. The platinum plate during the exhaustion is brought up to a red heat by electron bombardment from the filament, and the charcoal in the side tube is heated to the softening point of the glass, both processes being repeated until no more gas is given off.

The alkali metals introduced into the cells are prepared for use by a previous multiple distillation into glass tubes. Sodium and potassium are thus prepared in tubes of considerable length from which short pieces are broken off as required and placed in a three- or four-bulb distilling train attached to the photo-electric cell. Rubidium and caesium are distilled into short tubes with thin-walled bulbs at one end, and the thin bulb is broken after the tube is in the distilling system. By successive distillation the alkali metal passes from one bulb to another, each bulb being sealed off in turn, finally reaching a small bulb which is left attached to the cell. After the cell has been sealed off from the pump the alkali metal is melted and allowed to flow from this bulb to the bottom of the cell, where it forms a pool, from which, by gentle heating, it may be distilled on to the walls so as to present a large surface for evaporation. The platinum plate is then again raised to red heat by bombardment, which thoroughly cleans it from all large aggregations of alkali metal, and immediately on cooling it is ready for observation.

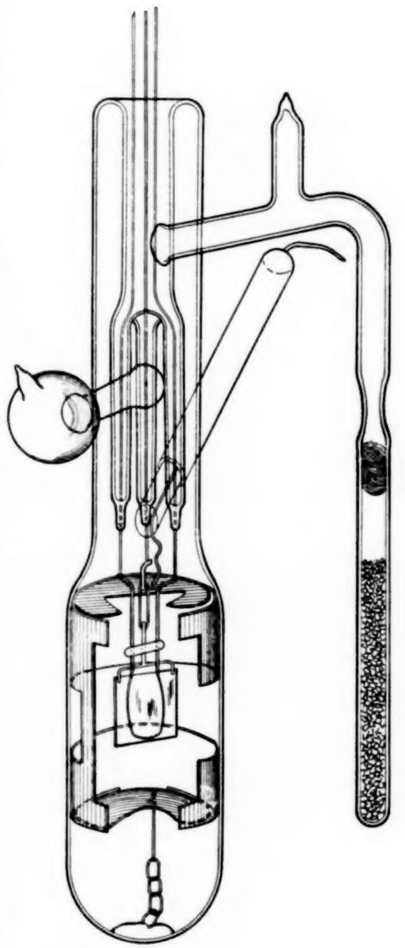

FIG. 1.—A typical form of photo-electric cell used.

MEASURING APPARATUS

The principal measurements made upon the cells consist of relative currents at various angles of illumination and relative

currents at various wave-lengths for the same intensity of radiation. For the angle measurements, a low-voltage, helical-coil tungsten lamp was mounted upon a radial arm which carried as well a nicol prism, whereby not only the angle of illumination, but the plane of polarization could be varied. The currents obtained with this apparatus were measured with a sensitive D'Arsonval galvanometer.

For the distribution of response through the spectrum a quartz monochromatic illuminator was used together with a quadrant electrometer arranged to measure the fall of potential across a xylol-alcohol resistance in series with the cell and batteries. A tungsten lamp, color matched with a black body at 2848°, was used as the light-source, and the deflections were reduced to equal energy values from a knowledge of the energy distribution of the source and the dispersion curve of the spectrometer.

RELATIVE SENSITIVENESS OF POTASSIUM FILMS ON DIFFERENT METALS

Two cells were made up, each containing four polished metal sheets on which potassium vapor was allowed to deposit spontaneously. The four metals in the first cell were gold, silver, copper, and platinum; in the second cell, nickel, tungsten, tantalum, and carbon.

The potassium films which form—as is immediately evident from the fact that all these surfaces become photo-electrically sensitive, although none of them are so to visible radiation without the presence of potassium—appear to have no effect on the color or surface character of the underlying metal, except in the case of gold. This latter becomes dull and olive brown in color and can only be cleaned off by a vigorous electronic bombardment, the effect of which lasts only for a few hours.

In Figure 2 are shown the photo-electric currents obtained from these eight potassium-coated materials for various angles of illumination, with the light polarized with the electric vector parallel and perpendicular to the plane of incidence (designated by the symbols $\|$ and $\perp$ respectively) and for light of two colors—yellow and blue, as obtained by interposing colored glasses between the light-source and the cell. The most striking feature exhibited by these curves

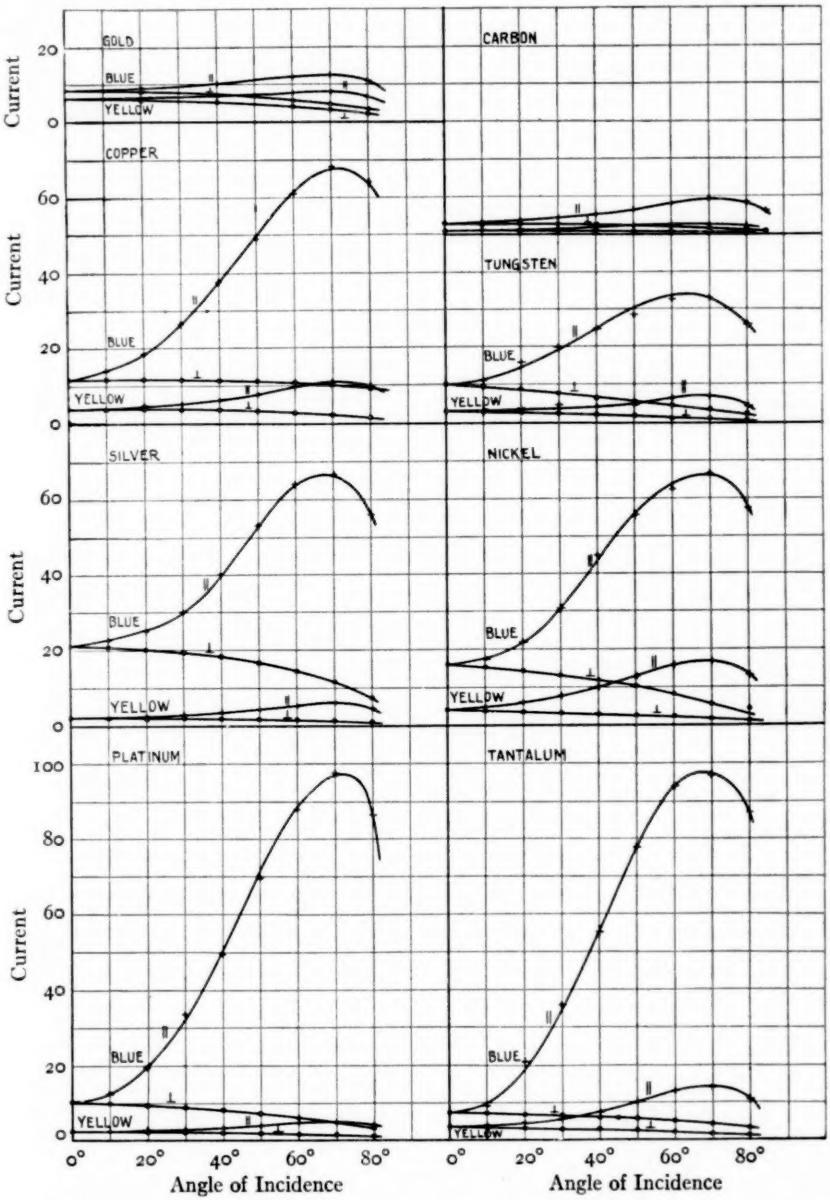

FIG. 2.—Photo-electric emission from thin film of potassium on several metals and carbon for illumination at various angles of incidence.

is the occurrence with most of the materials of an enormously enhanced emission for high angles of incidence, for light polarized with the electric vector parallel to the plane of incidence. This enhancement, which corresponds in some cases to ratios between the two planes of polarization of as high as fifteen to twenty-five fold will be recognized as the occurrence of the *selective photo-electric*

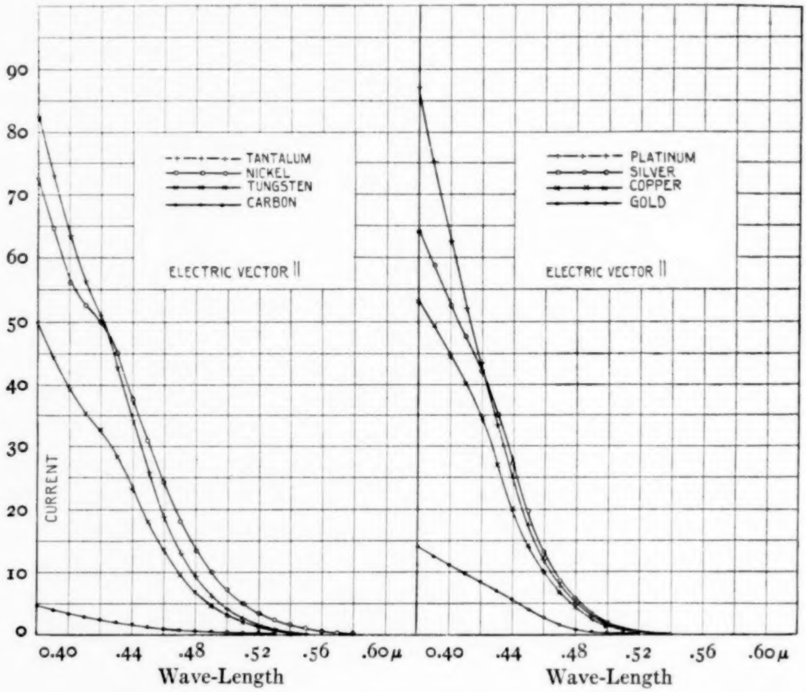

FIG. 3.—Wave-length distribution of emission with light polarized parallel to plane of incidence for thin film of potassium on several metals and carbon.

effect, which was discovered first in the liquid alloy of sodium and potassium. It will be noted that the extent of this selectivity varies greatly with the metal on which the potassium is deposited. In the case of gold, the selective character is entirely missing; in carbon it is questionable whether it is present; in silver the ratio of currents at 60° barely exceeds the figure "4," which is the limiting possibility for explanation by absorption. The magnitude of the photo-electric

current varies from material to material, irrespective of the ratio of normal to selective. In every case except nickel the selective characteristic where present is much more marked for blue than yellow light. In Figures 3 and 4 are shown the wave-length distributions of photo-electric current for these same materials for the two planes of polarization. In these two figures the shapes of the curves are

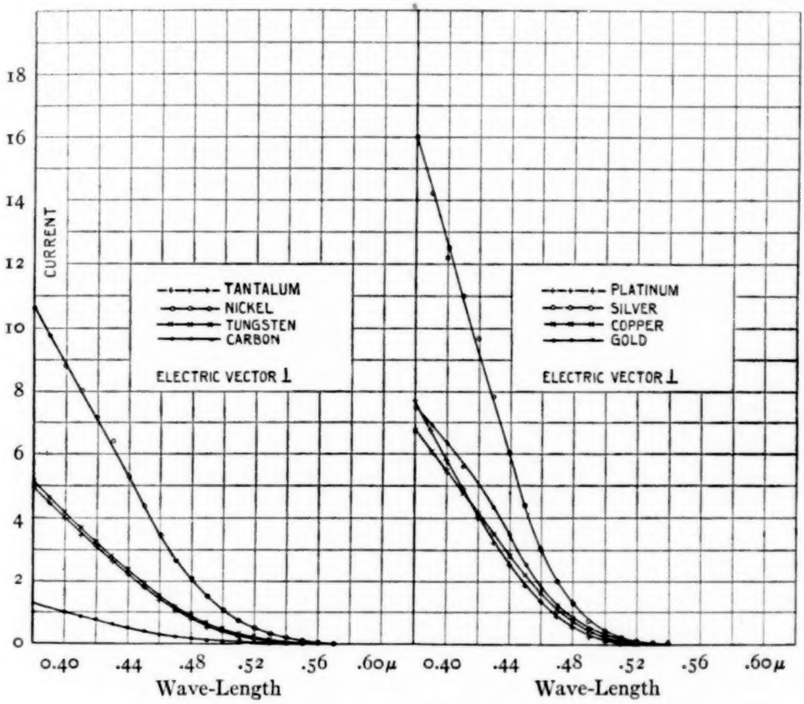

FIG. 4.—Wave-length distribution with light polarized perpendicular to plane of incidence for several metals and carbon, potassium coated.

alone to be considered, their values relative one to another are subject to some uncertainties due to difficulty in assuring the same angle of incidence and size of effective light-spot in all cases. There appears to be no marked dependence of the wave-length distributions of sensitiveness on the nature of the underlying metal except for the ⊥ plane where the data for gold, silver, copper, and platinum apparently show the photo-electric sensitiveness varying in the

sense of the reflecting power of the underlying metal. The prominence of the selective effect appears to have no direct connection with the optical properties of the material. Thus silver, which has a higher reflecting power than platinum, nevertheless gives a smaller selective photo-electric effect.

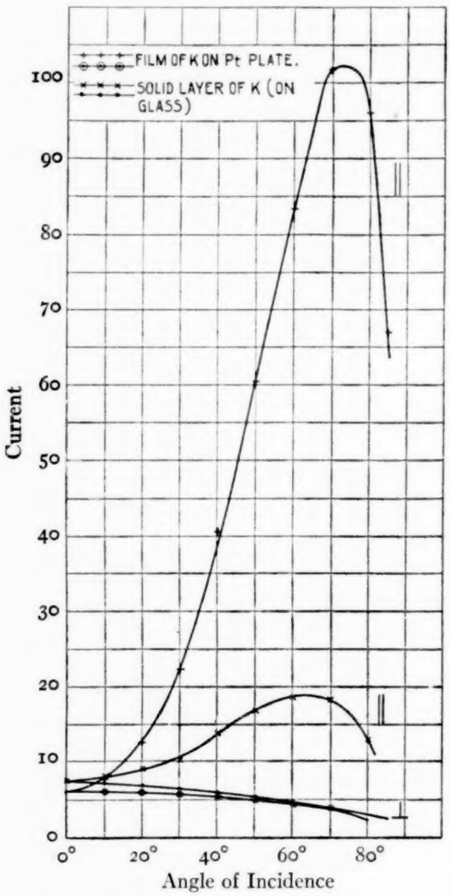

FIG. 5.—Photo-electric emission from a specular surface of solid potassium and from a thinly coated platinum plate for illumination at various angles of incidence.

An important point in connection with the sensitiveness of these thin films is to ascertain their relative sensitiveness with respect to thick, solid potassium. In order to learn this a special tube was constructed containing a bulb as the center electrode, one side of which was flattened and given an optically flat surface.[1] From an inclined side tube it was found possible to distil a thin opaque layer of potassium on this optical surface in such a manner as to form a specular coating of potassium. This specular character was lost after a few hours by a general reticulation of the surface, but it lasted long enough for the making of the necessary observations. In Figure 5 are shown the angle curves for this surface for white light, and on the same figure the corresponding curves for one of the thin films as formed on a polished platinum surface. It will be noted that the solid layer

[1] Ives, *Journal Optical Society of America*, **8**, 565, 1924.

is considerably less sensitive on the whole than the thin layer on platinum, the difference lying in the fact that the striking selective characteristic of the thin film is entirely missing in the solid layer. The ratio of emissions for the two planes of polarization is in the latter case about four to one at 60° angle of illumination, which is an amount which would not be incompatible with possible relative optical absorptions for the two planes of polarization (provided it does not exceed this value for any wave-length), whereas the ratio found in the true selective effect is not so explainable. This absence of a marked selective effect in bulk potassium will be made the subject of a separate paper.

PROPERTIES OF THIN FILMS OF DIFFERENT ALKALI METALS AS FORMED ON PLATINUM

In order to secure comparative data on the several alkali metals, these were all studied in cells having polished platinum plates as the foundation for the film. As is shown by Figure 2, the most striking characteristics of the thin films in the case of potassium are found with platinum as the base, as it lends itself readily to the necessary high polish and preliminary cleaning by electronic bombarding.

SODIUM

The phenomena exhibited by sodium films are comparatively easy to study for the reason that these films accumulate very slowly, requiring a matter of hours instead of the few minutes which suffice ordinarily with potassium. Figure 6 shows a series of angle curves for the two planes of polarization with "white" light, as obtained with sodium. It will be noted that the photo-electric sensitiveness rises to a maximum as the film accumulates and then decreases to a final value which is considerably less than the maximum previously obtained. The selective effect is well marked. Upon plotting the ratio of emission for illumination under the two directions of polarization at 80° incidence (Fig. 7) it is found that this ratio goes through a maximum which occurs considerably later than the maximum of sensitiveness. Figure 8 shows the wave-length distribution curves for light incident at a steep angle for the two planes of polarization at various periods

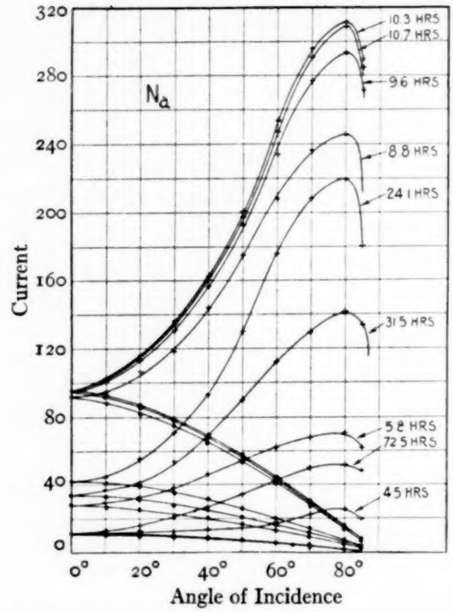

FIG. 6.—The progress of normal and selective photo-electric effects with time (after plate was cleaned off), sodium film on platinum plate; illumination at various angles of incidence.

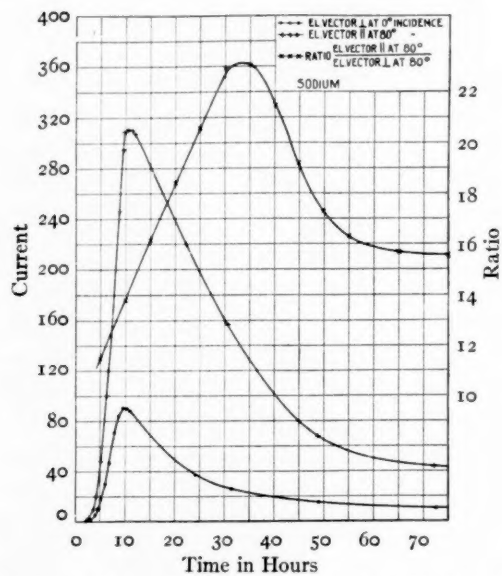

FIG. 7.—The progress of normal and selective photo-electric effects with time (after plate was cleaned off); sodium film on platinum plate, illumination at 0° incidence "normal" and 80° incidence "selective" and the ratio of these at 80° with time.

during the life-history. The significant points to notice are first, that in the earlier stages of deposition there is no noticeable difference in the shapes of the two curves. Second, that the long-wave limit of the emission first moves toward red as the film increases in thickness and then, after the maximum of photo-electric sensitiveness is passed, moves back toward the violet. Third, that

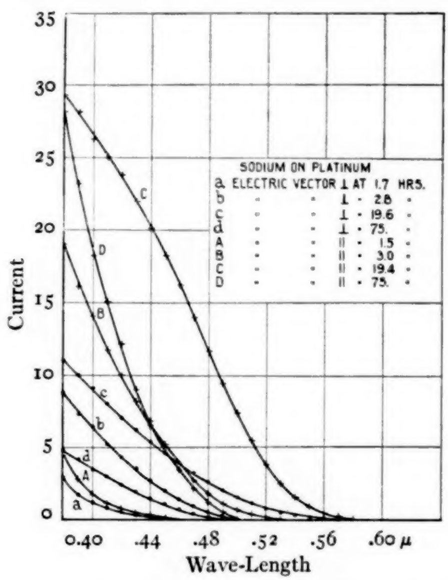

FIG. 8.—The progress of normal and selective photo-electric effects with time (after plate was cleaned off); sodium film on platinum plate; wave-length distribution.

where the curves are most different in shape, at the time when the differentiation into normal and photo-electric effect is becoming most marked according to the angle curves, the selective curve has the appearance of approaching a maximum somewhere in the near ultra-violet.

The cycle illustrated by Figures 6, 7, and 8 can be repeated indefinitely upon heating and cooling the plate. The phenomena exhibited, as is the case with all those described in the paper, are of this definite reversible character.

POTASSIUM

The task of following the entire life-history of forming potassium films is rendered difficult by the rapidity with which these

build up. It has, however, been found possible to observe the characteristics of films of various thicknesses by the opposite process of evaporating the film off. For this purpose the cell is placed in a Dewar flask furnished with a transparent window. The flask is filled with liquid air and the filament behind the platinum plate is brought to incandescence for periods of a minute or more. The heat thus generated drives the potassium film off the platinum and

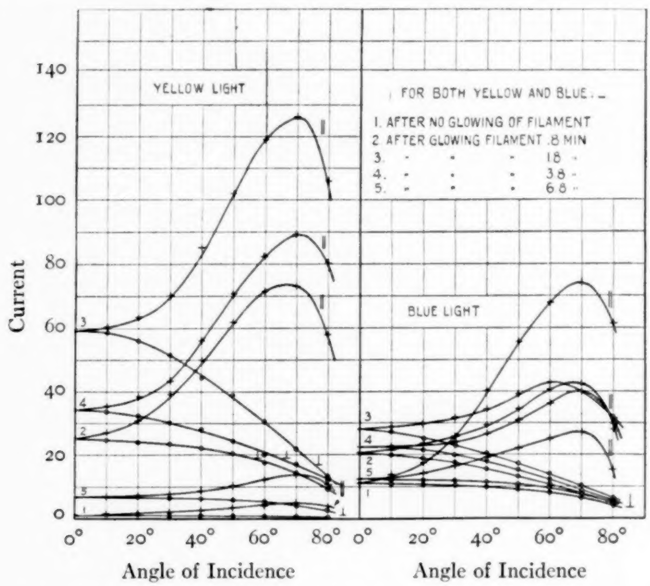

FIG. 9.—Photo-electric emission with yellow and blue light for illumination at various angles of incidence at different stages of evaporation of a potassium film on platinum plate.

the alkali metal is deposited on the sides of the cell. In Figure 9 are shown angle curves for the two planes of polarization and for colors yellow and blue, the successive curves showing the effects of repeated evaporations down to the point where the sensitive film is almost completely driven off.

The striking phenomenon here shown is the disappearance of the selective effect when the film is only slightly reduced in thickness below its normal value. It will be seen from the curves that what apparently happens is first, an increase in the normal effect for both

yellow and blue, accompanied by a decrease of selective emission for blue and a large increase for yellow (for "white" light the net result is that the selective emission stays nearly constant during this phase); this is followed by reduction of both effects for both colors as the thickness decreases. The curves corresponding to almost complete destruction of the film show for blue light practically the same values for the photo-electric current at zero angle of incidence as were exhibited under the initial conditions. On the other hand, the emission corresponding to illumination at an angle of 60° for the two planes of polarization shows a ratio of only two and one-half to one in place of the original value of over eight to one obtained with the cell standing in liquid air at the start of the measurements. In Figures 3 and 4 are shown the wave-length distribution curves for the emission from potassium films as present on platinum and other metals at room temperature. A point of importance is that the selective curves show no maxima in the visible spectrum. In particular they do not show a maximum at 0.43 μ where Pohl and Pringsheim found a maximum for colloidal potassium, which they assumed to be of the same sort as the maximum found in connection with the selective effect in the sodium-potassium alloy. If there is a maximum in the selective emission of these thin films it lies either at the extreme edge of the visible spectrum or in the near ultra-violet.

Wave-length distribution curves obtained from films after the platinum plate has been heated with the cell in liquid air, show first of all an extension of the long-wave limit out into the infra-red, and secondly, that the curves for the two planes of polarization are practically identical in shape; they correspond in character to the "normal" effect, confirming the conclusion drawn from the angle curves that the selective effect has been destroyed. The curves for potassium are not shown, as they are similar to certain of the much more complete series obtained with rubidium, described in the next section.

RUBIDIUM

Rubidium behaves in general in a manner very similar to potassium. Complete sets of angle curves were taken, but are not here shown as they exhibit very closely the same characteristics as those

shown by potassium. In order to obtain the behavior of the wave-length distribution curves with varying thicknesses of film, the special procedure was adopted of building a cell with a very heavy platinum plate ($3 \times 12 \times 18$ mm) which, after heating by means of a tungsten filament, took a long time to come to temperature equilibrium. The bottom of the cell was placed in liquid air during the process of heating the plate, and the air was allowed to evaporate spontaneously during the process of taking the measurements,

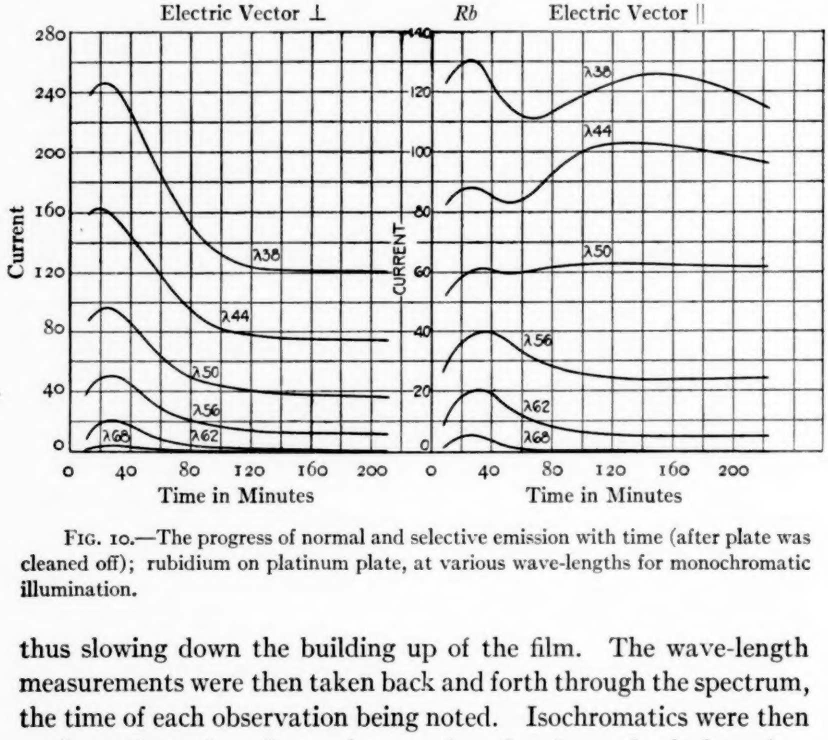

Fig. 10.—The progress of normal and selective emission with time (after plate was cleaned off); rubidium on platinum plate, at various wave-lengths for monochromatic illumination.

thus slowing down the building up of the film. The wave-length measurements were then taken back and forth through the spectrum, the time of each observation being noted. Isochromatics were then made against time for each wave-length. Several of these isochromatics are shown in Figure 10. From these isochromatics the complete emission curves according to wave-length were then constructed. Several of these (reduced to the same scale) are shown in Figures 11 and 12. It will be noted that the completely formed films (time $= \infty$) show a very great difference in magnitude between

the normal and selective effects, but that the selective effect does not exhibit any maximum at 0.48 μ, which is the position ascribed by Pohl and Pringsheim to the selective maximum for rubidium on the basis of their experiments with colloidal material. On the other hand, there is distinct evidence of a banded structure in the selective emission. There is a possibility (suggested by some other measurements not shown) of an absolute maximum at about 0.38 μ. As to the variation of the photo-electric emission with thickness of the film, it will be observed that as in the case of potassium the selective characteristic disappears when the film

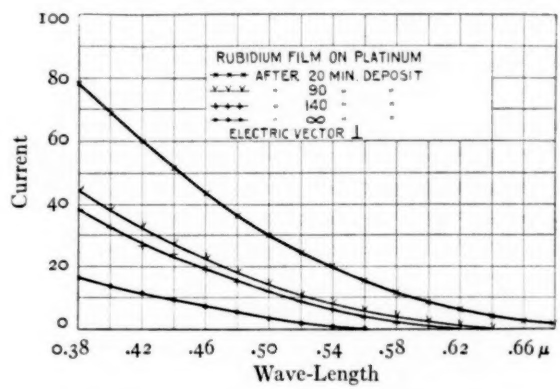

FIG. 11.—The progress of the normal photo-electric effect with time; normally incident illumination; rubidium film on platinum; wave-length distribution.

is reduced in thickness below the equilibrium it normally attains at room temperature. The selective emission at the blue end of the spectrum decreases continuously with decrease of thickness, but increases somewhat at the red end, while the normal emission increases everywhere. The result is that the two effects become not only alike in spectral distribution but approximate each other in magnitude. The long-wave limit moves from about 0.56 μ out into the near infra-red. It is also found as indicated by the isochromatics that when the thickness of the film is still further decreased (corresponding to only 5 minutes or less after the cessation of heating) the magnitude of the emission is decreased and the long

wave-limit moves back toward the violet, as in the case of sodium already described, and as is very well shown by the observations on caesium, which follow.

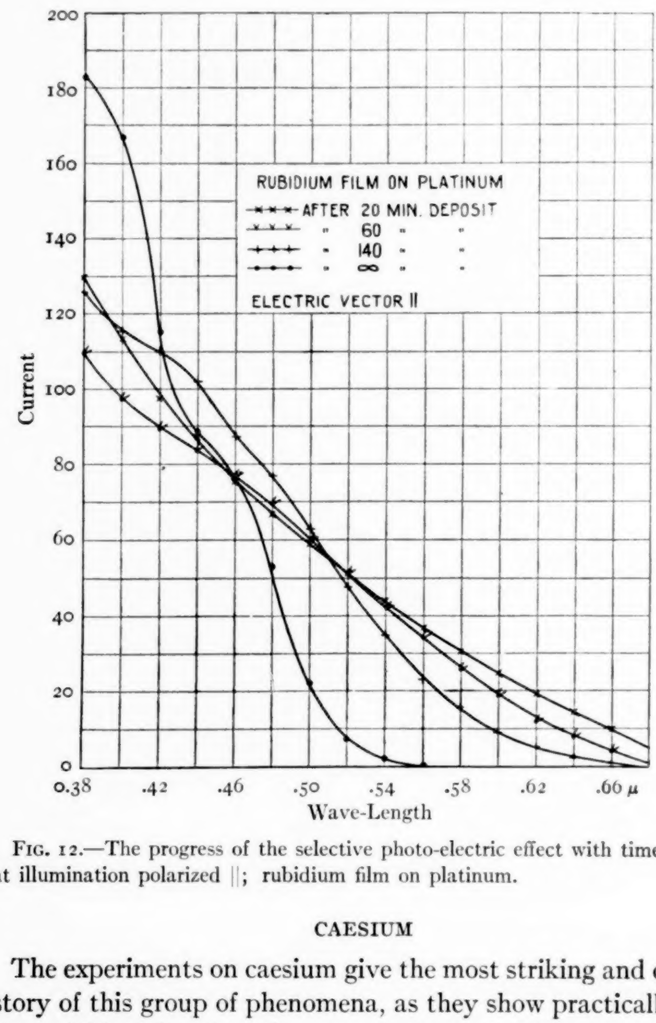

FIG. 12.—The progress of the selective photo-electric effect with time; 60° incident illumination polarized ||; rubidium film on platinum.

CAESIUM

The experiments on caesium give the most striking and complete history of this group of phenomena, as they show practically everything exhibited by the other metals, but in rather greater degree. Figure 13 shows the angle curves for two colors and both planes of polarization as the thickness of the film is decreased by evaporation to the walls of the cooled cell. It will be noted that with both

colors the emission due to light polarized in the || plane goes through a maximum at some thickness less than the one spontaneously achieved at room temperature. (This general increase of sensitiveness on evaporation is clearly exhibited on merely immersing the cell in liquid air, without any artificial heating of the plate.) It will be noted furthermore by comparison of curves 1 and 4 that the normal effect increases as the evaporation proceeds and that the

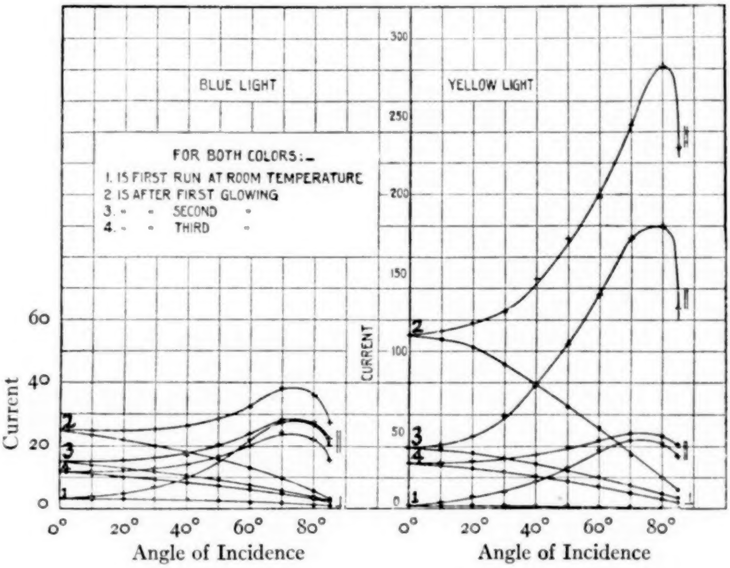

FIG. 13.—The progress of the normal and selective photo-electric effects with yellow and blue light at various stages of evaporation; caesium on platinum; for illumination at various angles of incidence.

selective effect (as defined by the ratio of emission for the || and ⊥ planes of polarization) is destroyed, as in the case of potassium and rubidium.

Figures 14 and 15 show wave-length curves all to the same scale made at successive points in the evaporation on to the cooled walls of the cell. The selective curves for the films accumulated at room temperature show some evidences of a banded structure. There is, however, no indication of a maximum in the neighborhood of 0.55 μ such as the formulae of Lindemann and others would indicate.

On decreasing the thickness of the film, the long wave-length limit moves toward infra-red and the normal and selective emission

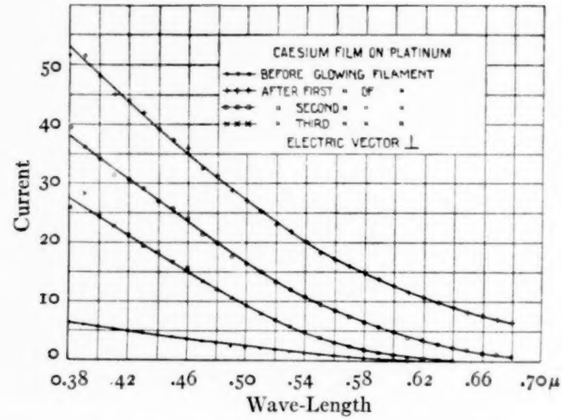

FIG. 14.—Wave-length distribution curves at various stages of evaporation—normal photo-electric effect; caesium film on platinum.

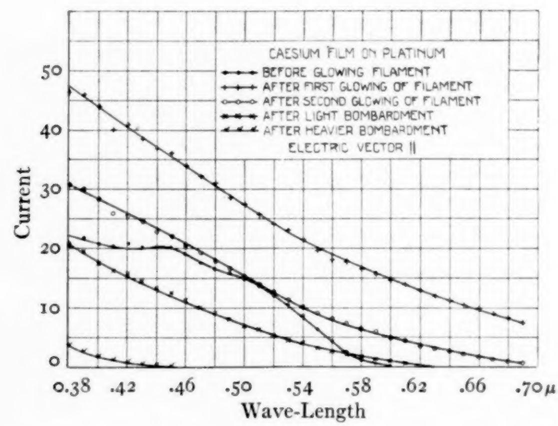

FIG. 15.—Wave-length distribution curves at various stages of evaporation—selective photo-electric effect; caesium film on platinum.

curves become identical in form, exhibiting a uniform slow rise from red to blue. When the film is reduced to minimum thickness the curves move again toward the violet.

VOLTAGE-CURRENT RELATION

The curves shown in most of the preceding figures were made at voltages of 80 to 100, which correspond to very complete saturation. A point of interest which demanded investigation was the behavior of the velocity distribution of emission of the electrons for various thicknesses of film. In order to investigate this, experiments were made on a potassium-coated cell with a tungsten plate at its center. Monochromatic light from a quartz mercury arc through a green

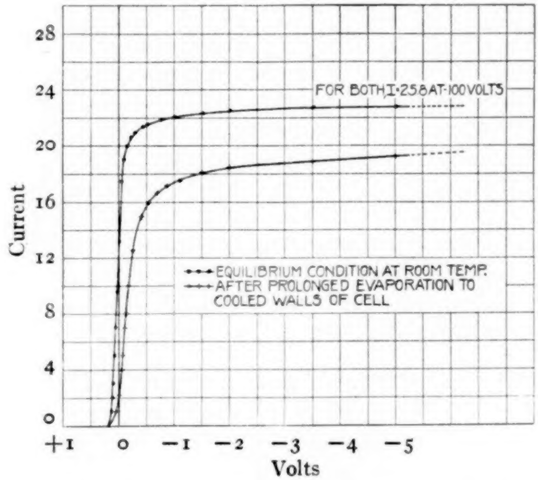

FIG. 16.—Voltage-current curves for thin film of potassium on tungsten plate; monochromatic illumination, λ 5461.

line filter was used. Observations were made first at room temperature, and then again, after the process of evaporation to the cooled walls had been carried so far that the emission due to the green light had increased and subsequently decreased to approximately its original value. The obtaining of the voltage current curves is greatly complicated by the fact that the walls of the cell are also sensitive. It was therefore necessary to obtain separately curves due to the illumination of the wall directly and then to correct the curves as obtained from the central platinum-plate electrode. A final corrected curve as thus obtained is shown in Figure 16. These curves, which are confirmatory of several others obtained previously with white light, show as their outstanding feature that

the film obtained after considerable evaporation and after the photo-electric emission has become entirely "normal" is much more poorly saturated than the ordinary emission curve.

Instead of the current attaining saturation at zero voltage, as is approximately the case for the initial film, the film as made thin by evaporation requires 50 volts or more to saturate. It might be expected that a contact difference of potential could exist between the thinly coated plate and the potassium-covered walls of the cell. This could, however, only shift the saturation point by two or three volts at most. The poor saturation observed indicates that it is necessary to apply considerable potentials to pull out the electrons which are loosened by light in these extremely thin, or possibly discontinuous, films. There is no clear evidence that any difference in stopping potential occurs as the film varies in thickness.

DISCUSSION

Although certain differences appear in the behavior of the several alkali metals as they form thin films by spontaneous deposition from their vapors, these differences are chiefly in the rate at which the cycle of phenomena appear, and the stage to which they advance under the same conditions of temperature and pressure. Essentially the phenomena presented by all the alkali metals are similar. Although two (sodium, rubidium) have been studied chiefly by watching the building up of the film on the underlying platinum surface, and the others (potassium, caesium) by observing the effects of evaporating the film, the phenomena, as certain check experiments show, are strictly ones of thickness, not affected by the directions of the change in thickness which is being produced. It is, therefore, permissible and convenient in making a generalized picture to consider the typical progress of events as the film builds up on the plate as this cools after being cleaned off by heating, as follows:

Immediately after heating, the plate is photo-electrically quite insensitive to light transmitted through glass. After a time photo-electric sensitiveness becomes evident. Observations at different angles of illumination, and in the two planes of polarization, show the emission due to the $\parallel$ plane to be not more than two to three times that in the $\perp$ plane, that is, there is no evidence of the selective effect. Observations of the spectral distribution of emission show

the emission for both planes of polarization to rise steadily toward shorter wave-lengths, the long-wave limit in the first emission observed lying well toward the violet. As the film gains in thickness the long-wave limit of emission moves toward the red, attaining a position much farther toward the infra-red than is exhibited by the film when thicker, or by a solid mass of the alkali metal. The emission curves for both planes of polarization are of the same form—that usually ascribed to the "normal" photo-electric effect—differing merely by the magnitude of the emission. At this stage the voltage-current curves show very poor saturation. As the thickness increases still further, the emission corresponding to the $\perp$ plane steadily decreases, that corresponding to the $\parallel$ plane decreases for the region of long wave-length, but remains nearly stationary for the short-wave region; simultaneously the long-wave limit moves back toward the violet. A point is ultimately reached where the emission in the $\parallel$ plane may be as much as twenty-five times that in the $\perp$ plane, that is, the selective photo-electric effect, as discovered by Elster and Geitel in the liquid alloy of sodium and potassium, is present. Examined according to the spectral distribution of emission, the selective effect exhibits indications of a banded structure, and in all cases probable maxima of emission at the edge of the visible or in the near ultra-violet spectrum. The maxima at 0.43 μ and 0.48 μ found by Pohl and Pringsheim in colloidal potassium and rubidium, or the maximum at 0.55 μ, predicted by Lindemann for caesium, are not present.

Following the films to still greater thickness, the magnitude of the photo-electric emission decreases again, the long-wave limit moves toward the violet, the selective characteristic becomes less marked. Upon carrying the film to such a thickness as to constitute an opaque specular layer (on glass) the selective characteristic disappears.

The chief interest of these observations probably lies in the light they will throw on the mechanism of the selective photo-electric effect. By "selective photo-electric effect" is here meant solely the emission at steep angles of incidence for light polarized with the electric vector parallel to the plane of incidence which is many fold (e.g., twenty-five times) greater as compared with the emission for

the other plane of polarization than possible differences in absorption can account for (four times). The typical example of this occurs in sodium-potassium alloy. The term "selective" has also been applied by Pohl and Pringsheim to the enhanced emission at one point in the spectrum found in colloidal deposits of the pure alkali metals, in the belief that it is essentially the same phenomenon, although their later work showed that in certain cases (e.g., specular calcium) a wave-length maximum of emission can occur without the true selective effect being present.

The observations here reported point rather definitely to the necessity for a certain state of aggregation of the alkali metal atoms before the selective effect appears. Thus with very little alkali metal present, when the selective effect is entirely absent, the atoms may be considered to adopt random positions or to be in isolated aggregates, not forming a continuous alkali metal surface. At this stage, the long-wave limit of emission is large, corresponding to a small surface work function ($w = h\nu_0$), and the voltage-current curve does not show the sharp saturation at zero field corresponding to a clear-cut work function. When, as the amount of alkali metal becomes greater, the surface work function becomes larger and the selective effect appears, the atoms may be considered as completely covering the surface, probably just covering it, and probably in a definite structural arrangement. For instance, the valence electrons may all be attached to the underlying metal (e.g., platinum), placing the photo-electrons in a specially favorable position for response to the properly directed electric vector of the incident light. Later, when the film becomes thicker, and the atoms pile up on top of each other, their special orientation is lost, and finally with a very thick film the selective effect again disappears.

ACKNOWLEDGMENTS

The writer is greatly indebted to Mr. Howard Weinhart, to Mr. G. R. Stillwell, and to Mr. A. L. Johnsrud for assistance in the preparation of the photo-electric cells and in making the extensive series of measurements recorded.

Research Laboratories of the
American Telephone and Telegraph Company
and the Western Electric Company, Incorporated
May 20, 1924

THE NORMAL AND SELECTIVE PHOTO-ELECTRIC EFFECTS IN THE ALKALI METALS AND THEIR ALLOYS

By HERBERT E. IVES and A. L. JOHNSRUD

ABSTRACT

The photo-electric currents from specular surfaces of molten sodium, potassium, rubidium, and caesium, and their alloys are studied at various angles of incidence for the two principal planes of polarization. The selective photo-electric effect is clearly exhibited only in the case of the liquid alloy of sodium and potassium. Wave-length distribution curves show maxima of emission, which are usually, but not always, most pronounced for light polarized with the electric vector parallel to the plane of incidence. The wave-length maxima previously assigned to the several elements are not confirmed; the maxima vary in position for the same element with the condition and mode of preparation of the surface.

INTRODUCTION

The first investigation of the photo-electric effect from specular surfaces of the alkali metals, with the incident light polarized in different planes, was made by Elster and Geitel, using the liquid alloy of sodium and potassium.[1] They made the remarkable observation that, while the photo-electric effect due to light polarized with the electric vector perpendicular to the plane of incidence shows a gradual diminution with angle of incidence—in the same manner that the absorption would decrease, as computed from the known optical constants of the material—the photo-electric current due to light polarized at right angles to this direction is enormously greater than can be accounted for by the relative absorption of light for the two planes of polarization. The maximum photo-electric current for light polarized with the electric vector parallel to the plane of incidence, which occurs at about 70° angle of incidence, was thus observed to be as much as seventy times greater than the current at the same angle for the other direction of polarization.

Pohl and Pringsheim[2] later investigated sodium-potassium alloy, carrying their observations through the spectrum. They found that the emission, with light polarized in the $\perp$ direction, showed a gradual rise toward short wave-lengths. On the other hand, the

[1] Elster and Geitel, *Annalen der Physik*, **61**, 445, 1897.

[2] Pohl and Pringsheim, *Verhandlungen der deutschen physikalischen Gesellschaft*, **12**, 215, 1910.

current due to light polarized in the || direction rose to a definite maximum at about 0.39 μ, this maximum becoming sharper and sharper the greater the angle of incidence. Pohl and Pringsheim applied to the photo-electric effects, due to these two planes of polarization, the terms "normal" and "selective."

In continuing their work Pohl and Pringsheim observed that rough, and particularly colloidal, sodium, potassium, and rubidium exhibited maxima in their spectral distribution of emission; these maxima falling at 0.34 μ, 0.435 μ, and 0.48 μ. Without actually producing mirror surfaces of the pure alkali metals they assumed that the maxima just mentioned were of the same nature as those found with sodium-potassium alloy, that is, that they were due to the component of the light polarized in the || direction as referred to the elementary surfaces of the rough metals. Subsequent work, however, showed that the presence of a maximum in the spectrum does not necessarily mean a selective effect in the sense in which this is exhibited by the specular surface of sodium-potassium alloy. Calcium, for instance, when formed into a mirror surface shows a spectral maximum of emission, but does not show the enormous enhancement of emission for steeply incident light polarized in the || plane.

PRELIMINARY RESULTS WITH SPECULAR SURFACES OF THE PURE ALKALI METALS

In an investigation which has been previously reported[1] on the photo-electric properties of extremely thin films of alkali metals as spontaneously deposited on polished surfaces of platinum and other metals, it was found that the alkali metals, sodium, potassium, rubidium, and caesium, all show in a striking manner the selective effect in the sense that this is exhibited by sodium-potassium alloy. The alkali metals under these conditions do not, however, exhibit the spectral maxima which were assigned to the various metals by Pohl and Pringsheim as the result of their studies of the metals in the colloidal state.

In connection with that investigation, the question was taken up as to how these thin films compare in sensitiveness with solid mirrors

[1] Ives, *Astrophysical Journal*, **60**, 209, 1924.

of the alkali metals. For this purpose the technique was developed of distilling a thin layer of potassium on the optically flat face of a bulb at the center of a large photo-electric cell. When the photo-electric effect of this potassium mirror was investigated an unexpected result was found, namely, that it did not exhibit the selective effect, the emission for the || plane never rising to more than three or four times that for the ⊥ plane. This observation prompted the present investigation, in which specular surfaces of the alkali metals and their alloys, one with another, have been studied. The method of obtaining the specular surfaces in this case, however, was by holding the metal molten, or, where possible, by selecting an alloy liquid at room temperature.

APPARATUS

The photo-electric cells used for this investigation were of the form illustrated in Figure 1. They consist of a bulb flattened on one side and attached to a rather long glass neck. One electrode consists of a wire entering the end of the bulb and reaching to the flattened bottom. The other electrode consists of a skeleton half-cylinder which is carried on a long glass stem within the neck.

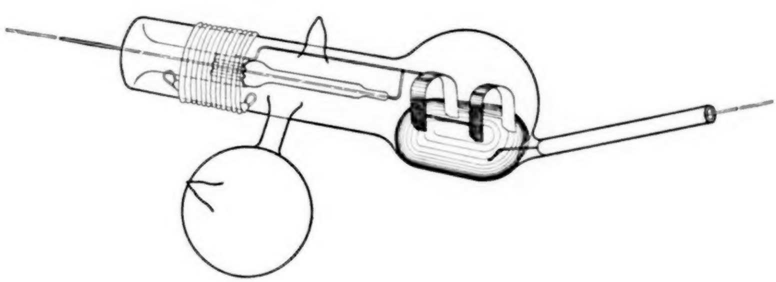

Fig. 1.—Form of photo-electric cell used for investigating normal and selective effects in alkali metals and alloys.

The alkali metal or alloy is introduced into a second bulb attached to the side of the stem, using the multiple distillation process described in previous papers. The pure alkali metals after distillation into the side bulb were melted and allowed to flow into the main bulb. In the case of the liquid alloys, an alloy of approximately the composition to give the lowest melting-point was formed

in the side bulb and allowed to stand until it showed segregation into floating crystals and liquid alloy. The liquid alloy was then poured off into the main tube.

The pure alkali metals are all solid at room temperature. The alloys of rubidium and potassium, also, are all solid at room temperature. Liquid alloys can be formed of sodium-potassium, sodium-rubidium, sodium-caesium, potassium-caesium, rubidium-caesium. The exact compositions of these liquid alloys have not been determined, but in the case of all except the sodium-potassium alloy the alkali metal of lower melting-point is considerably in excess.

Two series of observations were made on these metals and alloys. The first, which will be referred to as the "angle" curves, consisted of observations of the photo-electric current produced by illumination with "white" light when the light is incident at various angles to the normal, and the plane of polarization is either in the $\|$ or the $\perp$ direction. The apparatus used in making these observations consisted of a helical filament tungsten lamp carried at the end of a long arm rotating around a horizontal axis. On the same arm were carried a pair of plano-convex lenses, used to form an image of the lamp filament on the alkali metal surface, and a nicol prism between the two lenses, by means of which the plane of polarization could be controlled. Measurements of current were made with a sensitive d'Arsonval galvanometer.

The second series of observations consisted of measurements of the spectral distribution of emission for light incident perpendicularly on the metal surface, and for light incident at about 60°, with the plane of polarization in the $\|$ direction. These observations were made with a quartz spectrometer and a light-source of known energy distribution. Photo-electric currents were read by means of a quadrant electrometer which measured the potential drop across a high resistance in series with the cell.

The chief experimental difficulties were met in connection with the pure metals and the alloy, potassium-rubidium, which had to be maintained molten during the observations. This was a comparatively simple matter in making the angle curves, as these were made out in the open and were run through quickly enough so that an occasional flaming of the bulb maintained the molten condition

and kept the glass clear of deposited metal. In the case of the measurements made with the spectrometer, the whole apparatus had to be inclosed in a shielded, artificially dried box, and means had to be provided for maintaining the temperature of the molten metal, and, what was even more important, for keeping the walls of the cell free from condensed alkali metal. The procedure adopted was to apply an electric heating pad to the flattened bottom of the bulb and to place over the top of the bulb a grid of high-resistance wire through which a heating current was passed. An additional heating coil was placed around the stem of the cell in order to preserve the insulation which would otherwise have been destroyed by a deposition of alkali metal. The heating currents necessary in these various coils were determined by careful experiment so that the alkali metal was held molten but was not raised in temperature more above the melting-point than was absolutely necessary. One consequence of the use of the heating means just described is that, while in the angle curves the relative magnitudes of the different currents measured are substantially correct, the spectral-distribution curves are to be considered only with respect to shape and not with respect to magnitude, since the interposition of heating wires caused variations in the size of the incident spot of light.

ANGLE CURVES

In Figure 2 are shown together all the angle curves for the group of alkali metals and alloys. In this group it is to be noted that the curves recorded for the higher angles are probably somewhat too high, due to the scattered light from the spot on the wall illuminated by the light reflected from the metal surfaces. That is, the curves for the $\perp$ direction should probably drop down more at the higher angles of incidence instead of appearing nearly horizontal, as they do in several cases. The relative magnitudes for the curves of two directions of polarization are probably correct.

Examining the curves in detail the rather striking fact is found that, of all the metals and alloys, the only one which exhibits the selective photo-electric effect in marked degree is the sodium-potassium alloy, with which the effect was first discovered. In all the other cases the maximum ratio of photo-electric emission for the

two planes of polarization does not rise above three to five. While even this latter ratio is probably inconsistent with the known optical

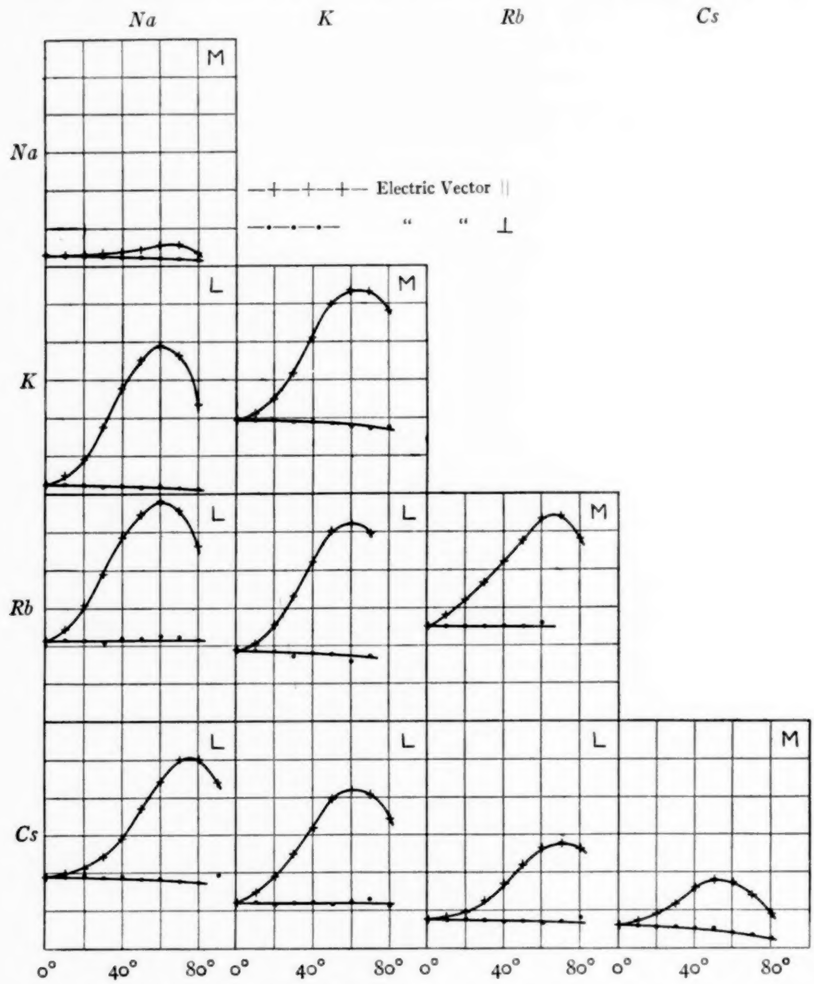

FIG. 2.—Photo-electric emission for various angles of illumination by polarized light; sodium, potassium, rubidium, caesium, and their alloys.

properties, it is, as a discrepancy, nevertheless of an altogether different order of magnitude from that shown by the sodium-potassium alloy, for which the ratio in the alloy shown is fifteen to one.

SPECTRAL-DISTRIBUTION CURVES

The spectral-distribution curves are shown together in Figure 3. A predominant characteristic of these curves is the exhibition of a maximum of emission at some point in the spectrum for the light polarized in the || plane. This maximum does not appear in sodium and sodium-potassium alloy, but as Pohl and Pringsheim's work has shown, it appears in the ultra-violet in the case of sodium-potassium alloy, and may therefore be present in sodium, in the same region. In the case of all the other alloys shown, however, there is a maximum which is located in all cases between about 0.42 μ and 0.48 μ. The location of the maxima for potassium, rubidium, and caesium at 0.435 μ, 0.48 μ, and 0.55 μ, as obtained from previous work, is not confirmed.

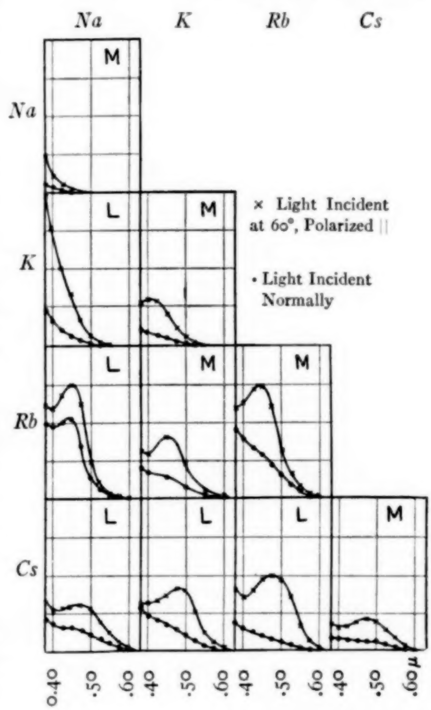

FIG. 3.—Spectral distribution of emission for normally incident and for steeply incident polarized light; pure alkali metals and their alloys.

It will be noted that the differentiation as to the shape of the curves between the normal and selective effects is less marked in many of the cases here shown than in the typical case (*Na-K*) studied by Pohl and Pringsheim. The alloys with caesium, for instance, do not show for the "normal" effect a uniform increase toward shorter wave-lengths, but show a definite tendency to reflect the selective maximum. This is particularly true of pure caesium. It is to be remarked in this connection that caesium has a decided yellow coloration which shows, to some extent, in its alloys. One of the alloys, namely, sodium-rubidium, is remarkable in that,

while it exhibits a prominent wave-length maximum, this maximum shows in both planes of polarization. In each of these cases where the two curves are not as different in shape as the similar curves for sodium-potassium alloy, the question is apt to arise whether this is not due to experimental errors, and specifically whether enough scattered light was not present in these cases to introduce a certain amount of selective into the normal curves. All evidence for this possibility appears to be negatived, first of all by the fact that careful observation showed the surface, when illuminated normally, to be practically free from any illumination except that falling perpendicularly on the surface, and secondly, by additional series of very careful observations with the sodium-rubidium alloy, using a narrow beam of light with which great care was taken to see that none fell anywhere except at the center of a pool of considerable size. It appears that this particular alloy is another example of the kind given by Pohl and Pringsheim (in calcium) of a material which exhibits a maximum in the spectrum which does not depend upon the plane of polarization of the light.

DISCUSSION

While the alloys of the alkali metals of all possible compositions have not been studied, it is nevertheless evident from this investigation that the pronounced selective effect discovered in the case of sodium-potassium alloy is a characteristic which is absent from not only the pure metals in bulk, but probably also from all the alloys except sodium-potassium. Such selective characteristics as the other alloys and the pure metals show consist in a conflict with the optical absorption properties to be represented by a factor of possibly two or three at the outside instead of fifteen or more, as is characteristic of the sodium-potassium alloy. This statement applies specifically to the ratios of the photo-electric currents for the two effects. The actual emission characteristics shown by the angle curves are not altogether such as the optical properties would predict, since the emissions for both planes of polarization are considerably higher at high angles of incidence than can be explained by absorption. Part of this—but certainly not all—is due probably, as already pointed out, to the form of the cells used.

On the other hand, as shown by the investigation reported in a previous paper, the pure alkali metals as spontaneously deposited on polished surfaces of other metals do show the selective effect in a most marked degree. The interesting question therefore is, What are the conditions under which the selective effect may be made to appear or disappear?

In the paper describing the photo-electric properties of thin films it was suggested that the selective effect is associated with a definite orientation of the alkali metal atoms with respect to the surface of the underlying metal. According to this view, the fact that the effect is missing with the bulk metals when they possess specular surfaces would mean that there is no definite orientation with respect to their surfaces. The behavior of sodium-potassium alloy becomes thus a special case for which it is necessary to assume that the atoms on the surface are taking up definite directions with respect to some characteristic axis of the atom.

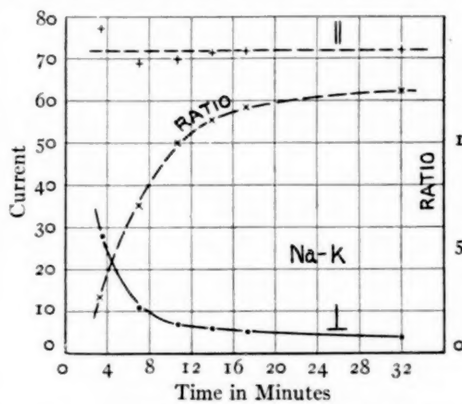

FIG. 4.—Normal and selective effects for steeply incident illumination in sodium-potassium alloy during the process of cooling from distilling temperature. Selective effect shown by symbol +. Normal effect shown by symbol ·. Ratio of two effects shown by symbol ×.

If this were the case with sodium-potassium alloy it might be possible to destroy this arrangement by disturbing the surface. One means of doing this would be to raise the temperature of the alloy. This experiment was actually tried. The whole bulb was raised to such a temperature that the alkali metal began distilling on the walls. The walls were then heated to drive the alkali metal off, and a series of observations of the photo-electric current for illumination at 60° to the normal and for the two planes of polarization was then made during the process of cooling. The results are shown in Figure 4. The selective effect, indicated by the crosses, remained

practically unchanged at all temperatures. On the other hand, the normal effect was very much higher when the alloy was hot, becoming less and less as it cooled. The ratio of the two effects when first observed with the hot metal was about two and one-half to one. This rapidly increased during cooling until the final value of fifteen to one was reached.

The relative behavior, during the process of cooling, of the emissions due to white light polarized in the two planes will be recognized as exactly parallel to that observed with thin films of potassium on platinum as these films build up from a condition of partial evaporation to their equilibrium condition at room temperature. The actual course of events in the latter case, as is made clear by observation through the spectrum, shows the substantial constancy of the "selective" effect for white light to be due to a counterbalancing of the general decrease in sensitiveness at long wavelengths by the growth of the real selective effect at short wavelengths. If the parallelism between the behavior of the *Na-K* alloy and the thin films of pure alkali metals is complete, we should expect observation by means of spectrally resolved light to show the disappearance of the wave-length maximum in the heated *Na-K* alloy, accompanied by an extension of the long-wave limit of emission. To verify this point satisfactorily, observations would be necessary well out into the ultra-violet, for which the equipment used in this study was not fitted. The similarity of the behavior of the selective effect, in the two cases, in so far as this experiment establishes it, gives support to the hypothesis that the selective effect is always ascribable to a peculiar orientation of the alkali metal atoms with respect to the surface.

Thus far this discussion has been confined to that selective effect which is evoked by light polarized in the $\parallel$ plane. As already noted, the term "selective" has sometimes been applied to the emission which shows a maximum at some point in the spectrum, in the belief that this maximum is always associated, as it actually is in sodium-potassium alloy, with the polarized-light effect. Consideration of these wave-length maxima is next in order. First of all, it is to be remarked that (Fig. 3), although these maxima usually occur in the emission due to the light polarized in the $\parallel$ plane, they are

sometimes present for both planes. Second, only in the one case of *Na-K* is this wave-length maximum associated with that enormous enhancement of the emission due to light polarized in the || plane which constitutes the true selective effect.

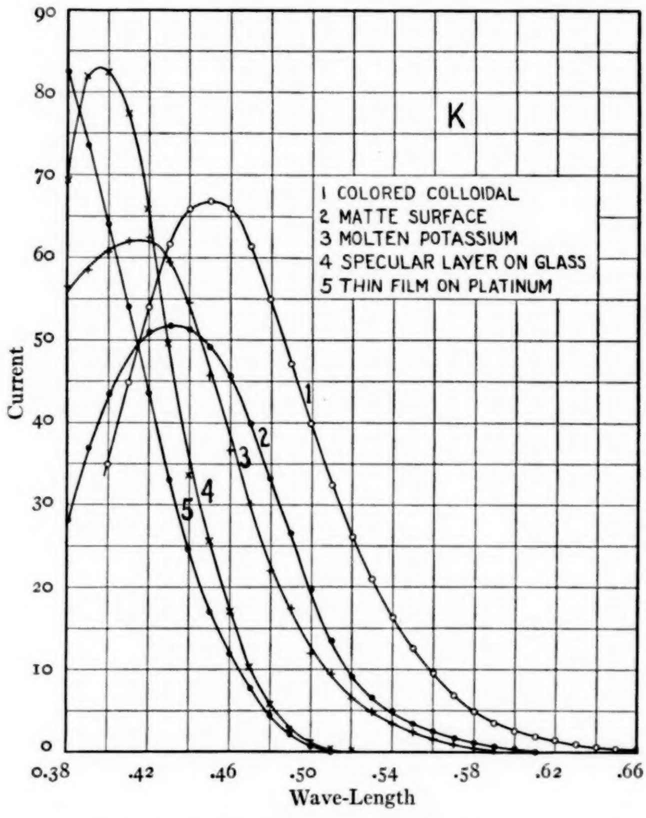

FIG. 5.—Wave-length distribution of emission from potassium surfaces of various types.

As to the position of the wave-length maxima, it has already been pointed out that these do not occur at the wave-lengths previously assigned by Pohl and Pringsheim and others. Further information on this point is offered by the wave-length distribution curves of Figure 5. These were all obtained with the same alkali metal, potassium, but each curve corresponds to a different surface

condition. Three of these (3, 4, 5) were specular, and the light was incident at approximately 60° and polarized in the || plane; two of these were rough, one uncolored, the other colored by a glow discharge. Only one (5), the thin film on platinum, exhibited the true selective effect. It will be observed that no two agree as to the position of the wave-length of maximum emission; the thin film on platinum, in fact, exhibiting no maximum in the visible spectrum: One generalization can however be made, namely, that the wave-length maxima of emission fall in exactly the same order as the long-wave limits. Thus the long-wave limits range from about 0.64 μ for the colored colloidal potassium to about 0.51 μ for the thin film on platinum, the wave-lengths of maximum emission from 0.45 μ for the colloidal potassium, to some point in the ultra-violet (if a maximum exists) for the thin film on platinum. This relationship between the wave-length of maximum emission and the long-wave limit is one feature of Richardson's theory of the photo-electric effect (his numerical relation $\nu_{max.} = \frac{3}{2}\,\nu_0$ appears to hold within the limits of uncertainty of the ν_0's for the curves of Figure 5, except for curve 4, for which the factor is nearer $\frac{4}{3}$). The large range of positions for both these wave-lengths suggests that while they are constantly related to each other, they are both functions of the surface conditions rather than constants of the material. Speculations connecting the wave-length of maximum emission directly with the atomic or crystal structure of the material appear in the light of these results to be of doubtful significance.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH COMPANY
AND THE WESTERN ELECTRIC COMPANY,
INCORPORATED
July 7, 1924

METASTABLE STATES IN LOW-VOLTAGE MERCURY ARCS

By MILTON MARSHALL

ABSTRACT

Current-potential curves for alternating and intermittent arcs in pure mercury between a hot filament cathode and nickel disk anode were obtained by use of a Braun tube oscillograph for pressures of from 0.001 to 10 mm with alternating voltages, the striking potential for 10 cycles and less was about 12 volts, but for frequencies of 10 cycles and above the current started at 3.0 volts and soon reached a saturation value until 8.0 volts, when a further increase was produced. To form the intermittent arc the voltage was periodically dropped from 15 to some lower predetermined value. If this lower value was less than 3.0 volts the arc was suddenly extinguished, at 3.0 volts the arc was maintained, and at 3.8 volts there was a sudden slight increase in arc current that was maintained for a very short time; at 8.4 volts the current was maintained at a higher current value. If 2 volts are added to the above observations, the results agree with the voltages corresponding to the $2p_1$ and $2p_3$ energy-levels and to the ionization potential of the mercury atom.

Evidence as to the lines of the two metastable forms of the mercury atom.—From spectroscopic data it has been suggested that the $2p_1$ and $2p_3$ energy-level of the mercury atom are metastable and remain in this condition for an appreciable time. The above results confirm this and give as a value for this time: for the $2p_1$ state 1/22 of a second, for $2p_3$ state 1/170 of a second.

Dependence of life of metastable mercury on pressure.—The critical frequency of metastable mercury ranged from 45 to 12 cycles in the pressure range from 0.08 to 1 mm. Above 1 mm the life was independent of pressure. This phenomenon is explained as due to collisions with impurities and diffusion from the arc space.

INTRODUCTION

One of the main approaches to the problem of atomic structure is by means of the observations of ionization and resonance potentials, especially since the development of Bohr's theory has led us to associate these electrical observations with the frequencies of definite spectrum lines. The direct observation of ionization and radiating potentials has been perfected by a great many observers. In this way a series of energy-levels are observed by electrical means and related with spectroscopic observations.

Another type of investigation that connects the spectroscopic data with electrical observations is the direct observation of metastable partially ionized energy-levels of the atoms. The existence of these states in helium was first suggested by Franck and Reiche,[1] and Franck and Knipping,[2] as an explanation of observations of the

[1] *Zeitschrift für Physik*, **1**, 154, 1920.

[2] *Ibid.*, **1**, 320, 1920.

photo-electric effect due to the radiation produced by electrons of various velocities. Spectroscopic series relations also suggest the existence of such metastable energy-levels. The existence of these metastable states in helium arcs was shown in experiments by Dr. F. M. Kannenstine,[1] and the energy required to ionize the state was found to agree with that predicted by spectroscopic data.

The following paper deals with experiments in mercury vapor carried out in a similar way to those of Kannenstine with helium.

EXPERIMENTAL METHOD

The arcs were formed in a pyrex tube between a hot filament cathode and a nickel disk anode. In some experiments tungsten filaments were used, in others oxide-coated platinum ribbon filaments, large enough to carry a current of about 6 amperes. Usually to form intense arcs 3–4 amperes were required.

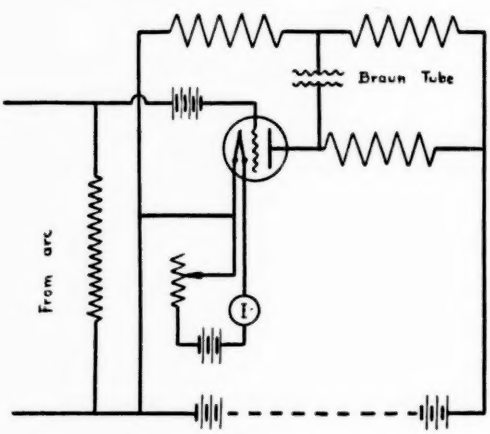

FIG. 1

The experimental tube was baked out at 500° C. by means of an electric furnace. The vapor pumps were kept running during this outgassing process and the filament was glowed at a high temperature. After the arc tube had cooled, the mercury was distilled into it from a small side tube which projected outside of the furnace.

A Braun tube oscillograph was used to observe the current and voltage across the arc. The arc current passed through the deflecting coils which gave a vertical deflection of the spot on the screen, while a horizontal deflection, proportional to the arc voltage, was produced by deflecting plates connected in parallel with the arc terminals.

[1] *Astrophysical Journal*, **55**, 345, 1922; **59**, 133, 1924; *Physical Review*, **19**, 540, 1922; **20**, 115, 1922; **23**, 108, 1924.

For most of the observations reported in this paper a 4 K.V.A. alternating-current generator was used whose frequency could be varied from 10 to 80 cycles. Occasionally a vacuum-tube oscillator was used for frequencies above the range of the generator.

It was found that the electrostatic deflection produced by the arc voltage impressed directly upon the Braun tube deflecting plates was so small as to make accurate observation difficult. The amplifying circuit shown in Figure 1 was therefore used in all experiments. This circuit was designed by Dr. F. M. Kannenstine for use in other experiments, and was found to work very well here.

In the first experiments ordinary mercury was used. In the later experiments especially purified mercury was kindly furnished by Professor W. D. Harkins. This mercury had been distilled a great many times in his experiments on isotopes.

EXPERIMENTS WITH ALTERNATING-CURRENT ARCS

When arcs were formed with an alternating e.m.f. the figure on the screen produced by the moving spot depended on the frequency. The type of curve obtained for a frequency of 10 cycles or less is shown in Figure 2 where the current deflection is vertical and the voltage deflection is horizontal. The arc struck at voltages between 12 and 20 volts, depending upon the pressure of the mercury vapor, the striking voltages being higher at the lower vapor pressures. A similar dependence of the striking voltage on the pressure is seen in the curves given by Richardson and Bazzoni,[1] and J. C. McLennan.[2] The striking voltage of the arc is probably that voltage at which sufficient ionization is produced to destroy the negative space charge around the cathode, thus allowing a great increase in the current through the tube.[3] When the pressure is very low the voltage must be raised much above the ionizing voltage in order to produce the ionization necessary to destroy this negative space charge. If almost sufficient ionization is present in the arc, due to some other cause, the additional ionization produced when

[1] *Philosophical Magazine*, **32**, 426, 1916.

[2] *Proceedings of Physical Society of London*, **31**, 30, 1919.

[3] K. T. Compton, *Physical Review*, **21**, 266, 1923.

the voltage reaches the *ionizing* voltage of the atoms may make the arc strike at that voltage.

After the arc was once struck[1] it was not extinguished at the striking voltage, as the voltage decreased but continued until the voltage had reached a value of approximately 3 volts as measured from the anode to the middle of the filament. This lower value of 3 volts was independent of the pressure of the mercury vapor. A slight decrease amounting to 1 volt or less was noticed with tungsten filaments when they were heated to extreme temperatures. This is probably due to increased velocity of emission from the hot tungsten.[2] No variation was noticed with oxide-coated filaments which were operated at a relatively low temperature. After the e.m.f. passed through zero it reached its negative maximum and returned, the arc again striking at the point *B*.

As the frequency was increased above 10 cycles a frequency was reached which Kannenstine calls the "critical frequency," at which the form of the curve suddenly changed from that shown in Figure 2. Then curves of the type shown in Figure 3 appeared. The arc struck when the potential on the arc had reached 3 volts (point *A*), and died out again before *B* was reached. With still higher frequencies the striking potential remained the same, but the arc was maintained for longer and longer times until curves similar to Figure 4 were observed.

Accompanying this change, the original striking voltage *B* decreased until it reached a constant minimum value of approximately 8 volts, indicated by *D* in curves 3 and 4. This change in the curves is very similar to that observed by Kannenstine for

[1] Smooth curves of the form shown in Figure 2 were not always obtained. As the mean arc current was increased certain parts of the curve became wavy. This same phenomenon was observed by Kannenstine in helium arcs, and indicated that the impressed voltage rose and fell during this striking period. He provisionally attributed this change in voltage to self-induction in parts of the circuit or to the presence of iron in the vacuum-tube oscillator, since the resistance in the arc circuit was very low. This phenomenon has been observed for a long time, particularly during the pumping of three electrode vacuum tubes in the process of manufacture. Since the publication of Kannenstine's paper this phenomenon has been investigated in detail by R. Bar, M. v. Laue and E. Meyer, and C. H. Eckhart and K. T. Compton, but these authors apparently are unaware that Kannenstine had already observed and reported this phenomenon.

[2] Y. T. Yao, *Physical Review*, **21**, 1, 1923.

helium arcs, and shows that a temporary modification of the mercury atom is formed which can be ionized at a much lower voltage than the normal mercury atom. The continuation of the arc down to 3 volts may be attributed to the presence of a metastable configuration. With a sufficiently high frequency the e.m.f. should pass from +3 volts to its negative maximum and back to +3 volts before the metastable mercury has disappeared, and upon reaching +3 volts the arc should strike, if sufficient metastable mercury is present. Since this critical frequency for pressures above 1 mm was 12 cycles, we may conclude that after approximately 1/24 of a second there is still sufficient metastable mercury present to cause an observable striking of the arc.

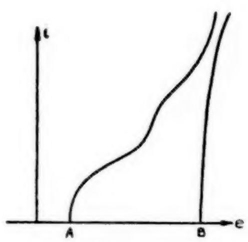

FIG. 2

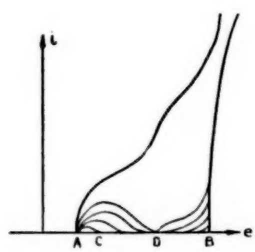

FIG. 3

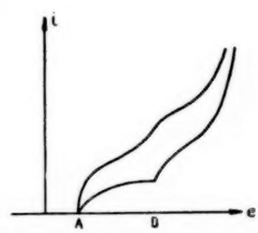

FIG. 4

The voltages given above must be corrected for emission velocities and contact differences in potential to give the actual velocities of the electrons. This correction is uncertain, but the behavior of the point D justifies us in identifying this voltage with the ionization voltage of the normal mercury atom, for, as mentioned above, when some ionization is already present a sudden increase in the arc current may be caused by the ionization produced at the ionization potential. The difference in the potentials corresponding to A and D was observed a great number of times and always found to be 5.0 ± 0.5 volts. This would indicate that the metastable state formed required 5.4 ± 0.5 volts to ionize it.

From spectroscopic data there are two electron configurations in the mercury atom which might be expected to be metastable.[1] These in spectroscopic notation correspond to the energy-levels

[1] Sommerfeld, *Atomic Structure and Spectral Lines*, p. 348; Foote and Mohler, *Origin of Spectra*, p. 102.

$2p_1$ and $2p_3$. Lines having the wave-numbers $2p_1-1s$ and $2p_3-1s$ have been observed as emission and absorption[1] lines, but the lines $1S-2p_1$ and $1S-2p_3$ have not been observed spectroscopically. This shows that if an electron is in either the $2p_1$ or $2p_3$ orbit to get to the $1S$ orbit it must pass through an orbit of higher energy-level. From spectroscopic data the energy required to ionize an atom in the $2p_1$ or $2p_3$ orbit is 4.96 and 5.73 volts, respectively. The accuracy of the experiments just described with alternating currents is not sufficient to decide whether it is the $2p_1$ or $2p_3$ state that is being observed. It would necessarily be that state which decayed at the slower rate. Later experiments will show that this is really the $2p_1$ state.

From Franck and Einsporn's experiments in which the $2p_1$ and $2p_3$ energy-levels are observed photo-electrically, it might be concluded that the energy-levels $2p_1$ and $2p_3$ are not metastable. Sommerfeld[2] says with regard to these experiments: "It is of particular interest that the transitions

$$1S-2p_1 \text{ and } 1S-2p_3$$

that are not observed optically and that are excluded by a selective principle governing the inner-quantum numbers make themselves noticeable in the current potential curve as bends. It occurs to us incidentally that the principle of selection, by the mode of its deduction, restricts only the phenomena of monochromatic emission, not the effects of electronic collisions."

However, if the atoms in the metastable states revert to normal in a fraction of a second the increases in the photo-electric curve observed by Franck and Einsporn would be expected, and this independent of whether the return is accompanied by the emission of the frequencies

$$1S-2p_1 \text{ and } 1S-2p_3$$

or of any other radiation which produces photo-electrons such as a band-spectrum due to a temporary reaction of the metastable atoms with atoms of an impurity.

[1] Metcalfe and Venkatesachar, *Proc. Roy. Soc.*, **100**, 149–266, 1921.

[2] *Atomic Structure and Spectral Lines*, p. 348.

In a paper on the duration of the 4.9-volt radiation in mercury, H. W. Webb[1] concluded that the radiation decayed exponentially with an exponential constant of 4000, and suggested that this might be due to the decay of a metastable state produced by the radiation. This rate of decay is so fast that these atoms would have had no effect on the results obtained.

To obtain an independent observation of the life of the metastable mercury, a commutator having three sets of segments was used. In this way a voltage of 15 volts was first applied to the arc, the arc was then short-circuited for a variable time, and, thirdly, a voltage slightly above that required to ionize the metastable mercury was applied. It was found that the arc restruck at the low voltage only when the time during which the arc was short-circuited was less than 1/22 to 1/24 of a second.

In the preliminary experiments ordinary mercury and a tube of soft glass having a soapstone plug to carry the leads into the tube were tried. The shape of the curve and the voltage obtained for the breaks were the same as in the experiments described above. But the critical frequencies were much higher in the preliminary experiments, the lowest frequency obtained varying from 40 to 120 cycles.

In the early experiments with the pyrex tube ordinary mercury was put into the tube and the whole baked out at 300° C. The lowest critical frequencies obtained were about 25 cycles.

These two sets of experiments would seem to indicate that impacts with impurities destroyed the abnormal mercury atoms, since increasing the purity lengthened the life observed.

DEPENDENCE OF CRITICAL FREQUENCY ON PRESSURE

It was observed at low pressure that the critical frequency was much higher than at pressures above 1 mm. The critical frequency was observed at various pressures and the values are given as the circles in Figure 5. The abscissae give the pressures in millimeters as computed from the vapor pressure-curve. The ordinates give the critical frequencies at which the first indication of striking at the low voltage was observed. This dependence of critical frequency on pressure is very similar to that found by Dr. F. M.

[1] *Physical Review*, **21**, 719, 1923.

Kannenstine[1] in helium arcs. The explanations given in that paper would also apply to the present experiments, that the abnormal mercury atoms may revert to normal by collisions with impurities or they may diffuse out from the arc space. At low pressure the diffusion becomes very important. In a short abstract, H. W. Webb and Lucy J. Hayner[2] also suggest that the persistence of the radiation of wave-length 2537A observed by them in mercury vapor

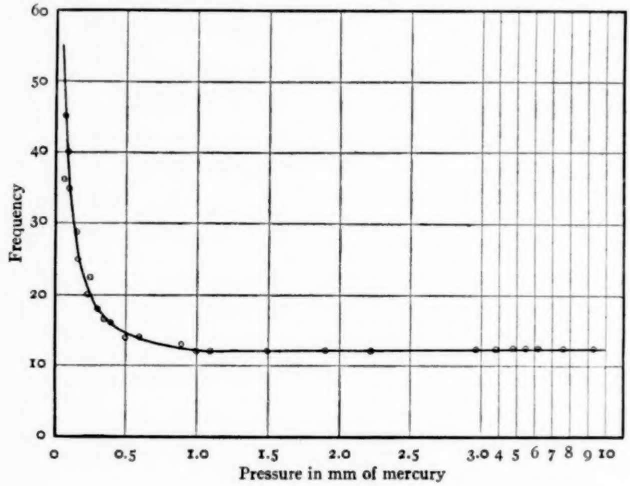

Fig. 5

can be explained on the assumption that radiation is carried to the surface by diffusion of the excited atoms. The full curve in Figure 5 is a calculated curve obtained by using the theory given by Professor A. J. Dempster[3] for Kannenstine's observations in helium. This theory deduces the relation between the pressure and frequency when the explanation just given for the decay of the metastable state is assumed. Taking the value for the radius of the experimental tube as 5 cm and assuming a diffusion coefficient for mercury,

$$D=41.8/p\ ,$$

where p is the pressure in mm, we find the following equation for low pressures:

$$f=9.23+2.77/p\ .$$

[1] *Loc. cit.*

[2] *Physical Review*, **23**, 294, 1924.

[3] *Astrophysical Journal*, **59**, 142, 1924.

For high pressures three terms of the series given in the paper referred to were used in computing the theoretical curve. It is seen that the agreement is very close at all pressures. From the kinetic theory we have

$$D = 1.2k/\rho\ ,$$

where ρ is the density. The coefficient of viscosity k for mercury has been determined by Koch[1] to be 500×10^{-6}. This gives a value for the diffusion coefficient

$$\mathrm{D} = 69.5/p\ ,$$

where p is the pressure in millimeters. This is slightly greater than that assumed above for the metastable mercury atoms. The deviation is in the direction that would be expected on a large radius of action for the metastable form.

ARCS WITH INTERMITTENT CONSTANT VOLTAGES

In order to obtain a more exact measurement of the voltages of the metastable states, and if possible to distinguish which partially ionized state was metastable, the ionizing potentials were observed by means of suddenly lowering the voltage on the arc to a predetermined low value. The circuit used is shown in Figure 6. The mercury interrupter (M) short-circuits a section BD of the resistance, causing the voltage to drop to a value which can be read on the voltmeter V. A uniform time-deflection was obtained by connecting the deflecting plates of the Braun tube to a potentiometer with a rotating contact which was fastened to the shaft of the inter-

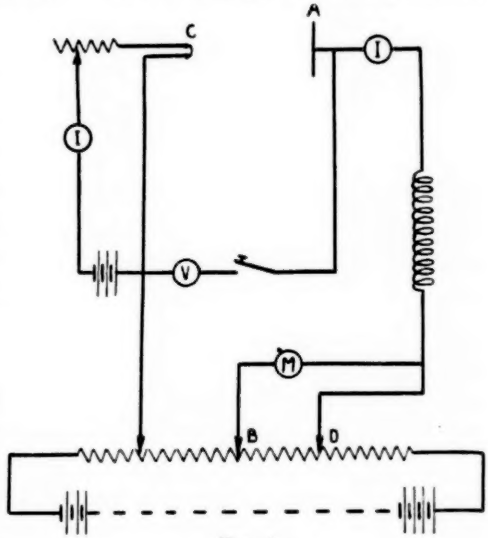

FIG. 6

[1] Wiedmann, *Annalen*, **173**, 857, 1883.

rupter. The first experiments were done with tungsten filaments and oxide-coated platinum filaments. Later an equipotential cathode was used.

With the lower voltage below 3.0 volts, two spots appeared upon the screen (Fig. 7) when the time-deflection was not used, the upper one corresponding to the arc current for 15 volts and the lower one corresponding to zero current. With the time-deflection no gradual transition could be observed between these two horizontal lines. When the lower voltage was increased to 3.0 volts the lower spot suddenly jumped to a position slightly above the zero axis (Fig. 8). With the time-deflection two current values were obtained. No curving of the lower line could be observed and neither could any decrease in the lower current value be noticed in the 1/80 of a second which was approximately the length of the

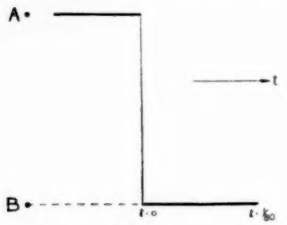

Fig. 7

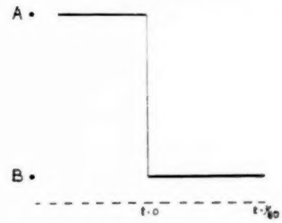

Fig. 8

time axis obtained on the screen. With a slight further increase in voltage the lower current increased until at 3.8 volts there was again a sudden change in form indicated in Figure 9. Without the time-deflection the lower spot suddenly developed a tail pointing upward, and the time-deflection showed that there was a gradual transition between the two currents. With further increase in voltage a third spot suddenly appeared between the two former ones, as is shown in Figure 10. The time-deflection shows that at this voltage the arc is maintained for a while before falling to the lower current value. This voltage corresponding to the appearance of this third spot was taken as the ionization voltage of the normal mercury; because with slightly higher voltages this figure went over into that of Figure 11 in which the arc was maintained at a current value corresponding to point *C*. Still further increases merely increased the lower arc current indicated by the raising of the point *C*.

The most natural interpretation corresponding to these various phenomena is that when the lower voltage (V_1) across the arc reaches that corresponding to Figure 8 we have ionization of the first most easily ionized metastable state of the mercury atom. When the voltage is increased to V_2 so as to give Figure 9 we have additional temporary ionization which may be regarded as due to a shorter-lived metastable state of mercury. The further increase of the lower voltage to V_3 corresponding to Figure 10 gives ionization of the neutral mercury. With an oxide-coated filament the actual applied voltages corresponding to V_1, V_2, V_3, were 3.0, 3.8, and 8.4, respectively. The first two values could be repeated with an accuracy of less than 0.1 of a volt, the third with an accuracy of approximately 0.2 of a volt. The actual electron velocities must be corrected for

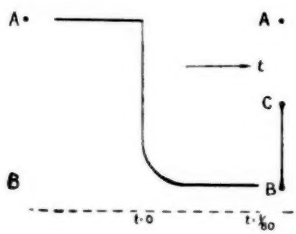

Fig. 9

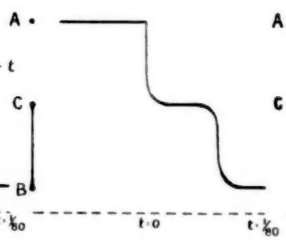

Fig. 10

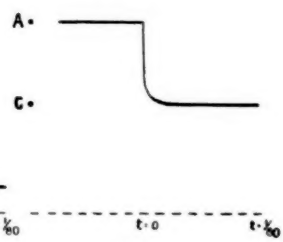

Fig. 11

initial emission velocity of the electrons, contact difference of potential, also for voltage drop down the filament. As it is not feasible to measure these we may avoid this correction by considering the differences between V_1, V_2, and V_3. If we identify V_3 with ionization voltage, viz., 10.4 volts, and apply this correction of two volts, we obtain 5.0 and 5.8 volts as the ionization voltages, respectively, for the two metastable forms of the mercury atom. Values agreeing within 0.1 of a volt with these values were repeated on a great many different occasions, with all pressures between 0.1 of a millimeter and 6 millimeters, although the observation of the ionization voltage was more distinct at vapor-pressures of 1–3 mm.

In an attempt to eliminate any uncertainty due to drop over the filament an oxide-coated platinum tube heated by an internal coil was used as cathode. With this the difference, 0.8 volts, was observed between the ionization potentials for the two metastable forms.

Theoretically, the ionization potential for the $2p_1$ state is 4.96 volts, and for the $2p_3$ state 5.73 volts. The agreement of the observations is as close as could be expected, and confirms the interpretation given above that the phenomena observed are due to successive ionization of the metastable states $2p_1$ and $2p_3$ and the normal atom. With tungsten filaments the difference between V_1 and V_2 was also observed and found to be 0.8 ± 0.1 volts. This agrees with the theoretical value 0.77 volt.

LIVES OF THE TWO METASTABLE FORMS OF THE MERCURY ATOM

As discussed in the first part of this paper, the time observed in the experiments with alternating current arcs applies to that metastable form which has the longer life. Evidently from the experiments with intermittent arcs the longest-lived metastable form is the $2p_1$ state and the value of 1/22 to 1/24 of a second given in the first of the paper applies to this state.

The time for the $2p_3$ state can be calculated from Figure 9. It is evidently much shorter than for the $2p_1$ state. The time axis was calibrated by measuring the rate of the mercury interrupter and calculating what fraction of a revolution produced the deflection observed. In this way it was found that the longest time at which any ionization of the $2p_3$ state could be observed was 1/170 of a second.

INFLUENCE OF SOME IMPURITIES ON THE LIVES OF THE TWO METASTABLE STATES

To test the influence of known kinds and quantities of impurities on the lives of the metastable states, carbon monoxide, carbon dioxide, nitrogen, water-vapor, and hydrogen were separately mixed with the mercury vapor. The partial pressures of these gases used had values ranging from 0.5 mm to 0 mm pressure as read on a McLeod gauge. The partial pressure of the mercury vapor during these experiments was 2.5 mm.

Observation showed that these gases in the range of pressures used had no influence on the life of the $2p_1$ metastable state, but did influence the life of the $2p_3$ state. The latter life was reduced from 1/170 of a second when no gases were present to 1/400 of a second

at the higher partial pressures of the foreign gases. The reduction of the life was practically the same for all gases used.

If impurities change the life of the $2p_1$ metastable form, as pointed out earlier in this paper, these impurities must be other than those listed. Experiments are still in progress to try and determine what impurities it is that change the life of the $2p_1$ state.

On one occasion a different type of curve was noticed, but it was found later that one of the tungsten seals had been cracked so that the different phenomena observed are provisionally ascribed to oxides. In this case when the voltage dropped to its low value the arc current fell for an instant to a lower value than shown in Figures 6, 7, 8, 9, and then rose to the values shown in those curves. Further experiments with impurities will be needed before this behavior can be interpreted.

The author wishes to thank Professor A. J. Dempster and Dr. F. M. Kannenstine whose help and suggestions have made this work possible.

Ryerson Physical Laboratory
University of Chicago
June 1924

PRELIMINARY EXPERIMENTS ON THE VELOCITY OF LIGHT

By A. A. MICHELSON[1]

ABSTRACT

Description of the method employed.—A beam of light from a Sperry arc at a station on Mount Wilson is reflected from one face of a rotating octagonal mirror to a mirror located on Mount San Antonio, about 22 miles away, whence it is reflected back to the originating station, where it is reflected by the next succeeding face of the rotating mirror into the micrometer eyepiece. The velocity of the light is ascertained from the rate of rotation of the mirror. The details and the formulae of the method together with a diagram are given. The advantages of the method are (*a*) greater distance between the stations, (*b*) sufficient light for accurate measurement, (*c*) elimination of the measurement of angles.

Preliminary results of experiments.—The distance between the stations as measured by the Coast and Geodetic Survey is estimated to be accurate to within one part in two million. The velocity of light as determined by these preliminary experiments is 299,820 km per sec., and this result is probably correct to one part in ten thousand. It is hoped that next summer the accuracy can be extended to one part in one hundred thousand.

The following investigation, by invitation of Dr. George E. Hale, then director of the Mount Wilson Observatory under the auspices of the Carnegie Institution of Washington, was begun in 1921. The following summers of 1922 and 1923 were spent at Mount Wilson in the endeavor to obtain the best conditions for a more accurate determination of the velocity of light.

These conditions are (1) a greater distance between the stations, with a maximum visibility of the return image; (2) sufficient light for accurate measurement of the position of the image; (3) elimination of the measurement of angle, thus reducing the actual observations to measurement of the distance between stations and the measurement of the speed of rotation of the revolving mirror.

The former measurement was undertaken by the United States Coast and Geodetic Survey under the direction of Major William Bowie, and it is estimated that the result is accurate to within one part in two million.

The stations selected were, for the home station, Mount Wilson, and for the distant station, Mount San Antonio, about 22 miles away, requiring about 0.00023 seconds for light to go and return.

[1] Research Associate of the Carnegie Institution.

During this time the octagonal revolving mirror making 530 turns per second will rotate through one-eighth of a turn, thus presenting the succeeding face to the return light at the same angle as though it were at rest.

The observation will then consist in obtaining this speed, in the present case by stroboscopic comparison with an electric fork making 132.25 vibrations per second, the latter being controlled by comparison with a free seconds pendulum, which last is compared with an invar gravity pendulum furnished and rated by the Coast and Geodetic Survey. When the reflections of the revolving mirror in the mirror attached to the fork are stationary, the observer measures the very small[1] angle α_1 to the zero.

The direction of rotation is then reversed and a similar measurement α_2 is made, thus eliminating the measure of the zero, and giving for the double "deflection" of the return image

$$2\phi=\pi-(\alpha_1-\alpha_2)=16\pi nD/V\ ,$$

whence

$$V=\frac{16nD}{1-\beta}\ ,$$

where

$$\beta=\frac{(\alpha_1-\alpha_2)}{\pi}\ ,$$

n = number of rotations per second, and D = length of light-path.

The figure represents the arrangement of the apparatus at the home station. Many other modifications were tried before the final adoption of this arrangement (or with a slight alteration which permits the final reflection from the octagon at nearly normal incidence), the chief merit of which is to eliminate direct reflections as well as diffuse light. These were tried during the summer of 1923, including the arrangement just described, but haze and smoke from forest fires prevented even such preliminary observations as would indicate the feasibility of the method—which would be determined by the intensity of the return image while the mirror is revolving.

[1] The angle $\alpha_1-\alpha_2$ was of the order of 0.002, so that an accurate knowledge of the "radius" was unnecessary.

This uncertainty was eliminated by the observations in June and July of this year, which showed an abundance of light, even on days which were unpromising. Another important point which was satisfactorily settled in these observations was the steadiness and sharpness of the return image. During the hour after sunset this was at times so small and distinct that its position could be measured to the hundredth of a millimeter. This, with a "radius" of 250 mm[1] giving a total "displacement" of 392 mm, would correspond to an order of accuracy of nearly one in forty thousand.

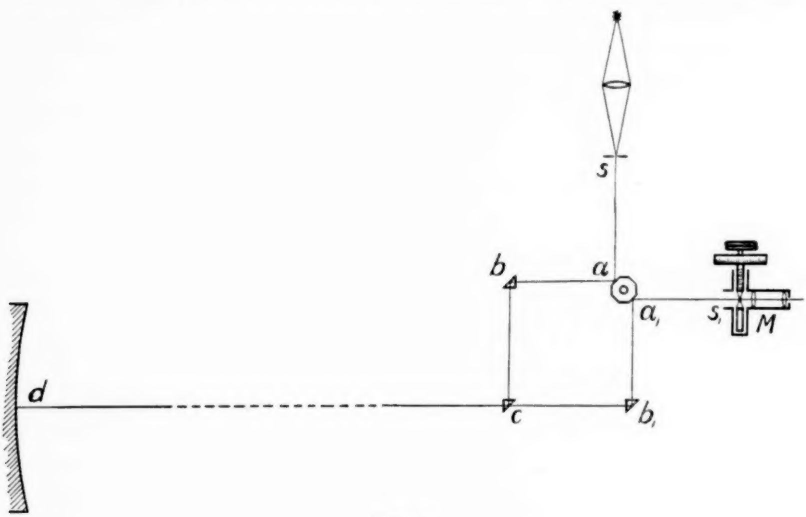

FIG. 1

Even on ordinary occasions when the "seeing" was less perfect the position could still be measured to 0.03 mm.

The light-source is a Sperry arc, which is focused on the slit *s*. Falling on the face *a* of the octagon, the light is reflected to a right-angle prism *b* to another at *c*, whence it proceeds to the concave mirror *d*, of 24-inch aperture and 30-foot focus. This reflects the pencil as a parallel beam to the distant mirror (also a 24-inch, 30-foot concave), proceeding thence to a small concave reflector at its focus. An image of the slit is formed at the face of this small

[1] The intensity of the image varies inversely as the cube of the "radius," which accounts for the rather small value actually used.

reflector, which necessitates the return of the light to the concave at d,[1] whence it passes over the prism at c to b_1, whence it is reflected to the face a_1 of the octagon, forming an image at s_1 where it is observed by the micrometer eyepiece M.

The program in the observations from August 4 to August 10 was as follows:

The rate of the electric fork in terms of the free auxiliary pendulum is measured shortly after sunset by counting the number of seconds required for a complete cycle. If P_1 is the period of the auxiliary pendulum and C the number of seconds in the cycle, then the number of vibrations of the fork per second will be

$$N=\frac{N_1}{P_1}+\frac{1}{C},$$

in which N_1 is the nearest whole number (in the present instance 133) of vibrations in one swing of the pendulum.

The auxiliary pendulum makes and breaks (by the passage of a platinum point through a mercury globule) the primary circuit of an induction coil, thus giving a spark reinforced by a condenser in the secondary, which is observed in a mirror attached to the fork. The Sperry arc is then put in action and focused on the slit (width varying from 0.5 to 0.1 mm). With proper adjustment[2] the return light is observed in the eyepiece as a brilliant starlike image. The valve for the air blast is then opened until the pressure near the nozzle is about 40 cm of mercury, when the image reappears in the field. The speed is regulated by a valve controlling a counterblast, until the stroboscopic images (four slowly moving images of one polished facet on the check nut of the revolving mirror) are just

[1] This is the arrangement also used in the method of Fizeau and Cornu, but so far as I know it was not supposed to be applicable to the method of the revolving mirror. It has given complete satisfaction, involving no other precautions but the careful focusing of the image on the face of the small reflector. It is true that this focus changes with temperature and causes a diminution in the intensity of the return beam, in the present instance of 1:8 for a change in focus of 3 mm.

[2] The adjustment is made shortly before sunset when the station at Mount San Antonio is well illuminated, by turning the revolving mirror until the image of the distant mirror is exactly in the middle of the slit. With this adjustment, as soon as the arc is focused at this point of the slit the light always returns; but slight adjustments of the slit or the arc may be necessary to obtain the maximum intensity.

stationary. At this instant the crosshair of the micrometer is made to bisect the image. The observations are repeated five to ten times, the direction of rotation of the mirror is then reversed and a similar series of observations is taken. The difference between the means of the two sets divided by the distance r (from crosshair to face of mirror) gives the angle $\alpha_1-\alpha_2$ of the formula. On completion of these observations the fork is again compared with the auxiliary pendulum, the mean between this and the previous determination being taken as the true rate of the fork in terms of the pendulum.

The true rate in seconds is found by comparing the auxiliary pendulum with an invar pendulum furnished and rated by the United States Coast and Geodetic Survey[1] by counting the number of seconds in one cycle of the image of the spark given by the auxiliary pendulum as viewed in the mirror attached to the invar pendulum.

Following is a summary of results:

TABLE I

Date	P_1	N/P_1	$1/C$	$\alpha_1-\alpha_2/\pi$	K
August 4	1.00630	132.16	+0.07	+0.00020	132.20
August 5	1.00630	132.16	−0.03	−0.00060	132.21
August 7	1.00622	132.17	.04	.00054	132.20
August 8	1.00628	132.16	.01	.00070	132.24
August 9	1.00633	132.16	.01	.00040	132.20
August 9	1.00633	132.16	.01	.00050	132.22
August 10	1.00635	132.16	00	.00020	132.19
August 10	1.00635	132.16	−0.05	−0.00030	132.15
Mean	....	....	....	....	132.20±.006

$V=64KD$

$D=35385.5+40.8^2=35426.3$ m

Final result:

$V_1=299735$ km per sec. in air

$V=299820$ km per sec. *in vacuo*

[1] This measurement was carried out by Lieutenant Donal Pheley, of the United States Coast and Geodetic Survey.

[2] 35385.50 = distance between C.G.S. marks

30 ft. = focal length of mirrors

12 ft. (provisional) = distance from C.G.S. marks to focus of mirrors

$4\times30+2\times12=144$ ft. $=44$ m

Correction 3.2

40.8m

These results, though provisional and to be supplemented by a more careful and more extended series of measurements contemplated for the summer of 1925, are probably correct to within one part in ten thousand.

The principal source of error was found to be in the maintenance of sufficiently constant speed of the revolving mirror. This was doubtless due to lack of proper provision for a constant pressure of the air blast and not to any lack of precision in the measurements of the displacement of the image. This difficulty will be eliminated in the work for next summer, when, it is hoped, the uncertainty of the result will be reduced to one in one hundred thousand.

RYERSON PHYSICAL LABORATORY
UNIVERSITY OF CHICAGO
October, 1924

Reviews

Eclipses of the Sun. By S. A. Mitchell. New York: Columbia University Press, 1923.[1] 8vo, pp. xvii+425, 59 illustrations. \$3.85.

This finely printed and well-illustrated book will prove a very welcome addition to the list of handbooks covering special fields of astronomical science. It is a most readable treatise for the layman or the amateur astronomer; there are, in addition, many portions of the book which, through the convenient and exhaustive compilation of past results and present theories, will prove a very useful, in fact an indispensable, manual of reference for the professional astronomer and the eclipse observer.

The work opens with two chapters devoted to ancient eclipses and two treating the subject of the prediction and the verification of eclipses in its more general rather than in its computational aspect.

The list of eclipses given on page 56 is taken from that given in the *Encyclopaedia Britannica*, and unfortunately omits any reference to the eclipses of July 9, 1945, and June 30, 1954, an omission which is made more definite by the author's emphasis on the lack of total eclipses in the United States between 1925 and 1970. It would appear, from Oppolzer's *Canon der Finsternisse*, that the omission of these two eclipses is unwarranted. They should certainly be included in any discussion of eclipses crossing the continental United States within the present century.

Two sections are then used in a rather full treatment of the history of the spectroscope, and one chapter is given to the surface of the sun, as an introduction to the main theme of the book. Two chapters are employed in discussing the results secured from the observation of modern eclipses, after which three are devoted to an entertaining and popular account of the author's experiences at the four eclipses occurring in the years 1900, 1901, 1905, and 1918. The subject of the flash spectrum, as the field of work in which the author has been most interested, is very fully treated in the next two chapters, followed by one on eclipse spectra and related solar phenomena. The final third of the book discusses the theories of the structure of the atom, with reference to Saha's ionization hypothesis, theories of the corona and coronal structure, and the

[1] We understand that a new impression of this book will be issued at the end of 1924.—Editors.

Einstein theory, with a summary of eclipse results bearing thereon. The treatise is provided with a very good index; a number of stylistic lapses will be noted in the first three chapters, but typographical errors are rare. It is not an easy matter to combine in one book sections which shall be enjoyed by the general reader, together with technical chapters of use to the professional astronomer, but this has been well done, with a minimum of overlapping in two so diverse methods of treatment.

The scope of the book is far wider than can be indicated in the brief tabulation of a review; in fact, matter is occasionally introduced which some may regard as not strictly germane to the title. Present-day theories are treated conservatively and exhaustively.

The ungracious task of a reviewer in suggesting changes or additions is doubtless a light and easy matter compared with the labor of incorporating such changes. The work will prove so useful to the eclipse observer that the present reviewer wishes that a chapter might have been added on the "practical astronomy" of the eclipse camp, perhaps with the excision or abbreviation of some matter bordering on the extraneous, and in fine print, if necessary, that the layman might "skip." While the practical astronomy of the eclipse camp is theoretically the same as that of the books, in its details and in its application it is a thing apart. The meeting of its new and unanticipated problems has always constituted one of the keenest pleasures of the eclipse observer, not omitting the case of the astronomer who found, at his eclipse camp in the Southern Hemisphere, that the driving clock of his equatorial should have been adapted so as to turn his telescope in a direction contrary to that which it had north of the Equator. What lens should be used for coronal extension and what for coronal detail? Why is a two-piece lens unsuitable for Einstein tests? What are the formulae for a moving plate-carriage? What is the azimuth of a camera used with a coelostat, and at what angle with the horizon will then be the cusps? What is the quickest way to adjust a polar axis in the field, or to determine a focus? What exposures will be best for a well-rounded program, and what different emulsions will be of advantage?

The answers to these and to a hundred other practical eclipse questions are buried in the notebooks of a dozen modern eclipse expeditions; some are referred to incidentally in the present treatise. While the intending observer should be able, theoretically, to answer all such questions from his past experience or his inner knowledge, still a compact collection of methods, description and comparison of apparatus and lenses, and a tabulation of useful formulae would be a great convenience.

Heber D. Curtis

Relativity: A Systematic Treatment of Einstein's Theory. By J. Rice. London: Longmans, Green & Co., 1923. 8vo. Pp. xiv+397. $6.00.

The theory of relativity has in recent years been the object of great developments, and many books or treatises have been written on the subject. Some authors have tried to give popular expositions of the theory, but it is evident that it is impossible to bring out in that way the profound revolution which has modified our concepts of time and space and some of the principles of physics. Other expositions, of a rigorous character, are only accessible to students after they have acquired the preliminary mathematical knowledge necessary for the understanding of the theory. Mr. Rice has published this present treatise for the undergraduate student, who may wish to know something more than he can learn by reading popular pamphlets. The book is divided into three parts, with an introductory chapter: (1) "The Restricted Relativity"; (2) "The Generalized Relativity"; and a third part involving the geometrical conceptions which have led Weyl, Eddington, and Einstein successively and more closely to the homogeneous union of both the gravitational and electromagnetic fields. The method followed is, therefore, an inductive one; it gives the historical development of the theory from its appearance in 1905 until the latest generalization by Einstein himself in 1923.

1. The first part, divided in seven chapters, is the study of the restricted relativity or of the relativity of the electromagnetic field *in vacuo*, for two observers who are in rectilinear and uniform translation with respect to each other. The theory is based upon the derivation of the Lorentz co-ordinates of space and time for an event, the constant velocity of light being assumed. That transformation involves the invariance of the line-element $(ds)^2$; it forms a kind of code between the languages of the two observers, O and O', who observe the same event, each of them using his proper units of length and time. The equations lead immediately to the notion of simultaneity, and well-known consequences are: A rod moving with respect to an observer seems to be contracted in the direction of the motion; a clock in motion seems to run slower, etc. From the transformation of co-ordinates, the kinematics and dynamics of a particle can be fully developed. Immediate applications are the law of compound velocities, the explanation of the aberration of light and of Doppler's effect. The dynamics of a particle will be expressed in four equations of motion, the fourth being the equation of energy. The invariance of $(ds)^2$ involves the invariance of these equa-

tions; that means that the observers O and O' describe the motions by using equations having the *same form.*

The electromagnetic field is characterized by the well-known equations of Maxwell, generalized by Lorentz for material media. These equations expressed in terms of four vectors representing the electric and magnetic forces, the density of electricity, with respect to the co-ordinates and time, are the same for the observers O and O' when each of them uses his proper units; our code will allow us easily to transform into the language of O' what has been observed by O, and vice versa. The preceding can be extended to the dynamics of continuous media; it leads to the relativity of the laws of conservation, and the development of the equations shows the negative result of Trouton and Nobel's experiment, due to the fact that the momentum of a body has not, in general, the same direction as its velocity. The introduction of thermodynamic considerations shows the invariance of the entropy; but the temperature, on the absolute scale, varies from one observer to the other in the same manner as the volume. We have supposed that the motion of the two observers, one with respect to the other, falls along one axis. By successive Lorentz transformations, it must be possible to pass from the observer O to other observers O', O''; all these transformations forming a *group*, as has been shown by H. Poincaré, it is also possible to pass directly from O to O''.

2. The different chapters of this part, treating on general relativity, are the generalization of the corresponding chapters in the first part. That which was done there in the case of two observers who are in uniform and rectilinear translation with respect to each other is extended now to observers who have arbitrary relative motions. By analogy, the square of the line-element $(ds)^2$, representing the distance between two infinitely close point-instants, must be constant for *all* transformations of the co-ordinates x_1, x_2, x_3, x_4, used by O, into the co-ordinates x'_1, x'_2, x'_3, x'_4, used by O'. Many interesting examples of transformations are indicated. Hence the form of physical laws is the same in a gravitational frame and an ideal accelerated frame. The generalization of the equations of transformation leads to the introduction of vectors and tensors of three kinds, viz., covariant, contravariant, and mixed, which have to be carefully distinguished from one another. The starting-point of the new dynamics, in which the ideas of inertia and gravitation are united, is expressed by the fact that the natural path of a free particle is a geodesic line in space-time determined by the form of $(ds)^2$. This is considered here merely as a hypothesis, although it can be demonstrated that it has

really to be so in the case of a field produced by matter. In the same way, it can be demonstrated that the equation of a ray of light is a geodesic of $ds=0$. The study of the gravitational field leads to the determination of $(ds)^2$. This most general quadratic form of the second order contains now ten functions $g_{\alpha\beta}$ of the co-ordinates x_1, x_2, x_3, x_4, which are the ten gravitational potentials of Einstein. In the determination of these potentials we have to distinguish between geometrical solutions and natural gravitational fields; this criterion is given by "Einstein's law" in the gravitational field, which under certain conditions degenerates into Poisson's equation. It is the simplest law in this tensor analysis. Mr. Rice gives first Einstein's original method for determining the gravitational equations, based on certain considerations of covariance. Later on he deals only with the derivation of these equations from the principle of stationary action (Hamilton) as it has been done by Lorentz, De Donder, Hilbert, and Einstein himself. This enables him to write all equations in the form of Lagrange. But, previously, he shows how the equations of the electromagnetic field have to be generalized so that their form shall be invariant for all transformations of co-ordinates; and he then works out the general covariant form of the equations of momentum, energy, and mass. Finally, as an application, he deals with the case of the field of a particle and its well-known astronomical consequences. The propagation of gravitational waves is considered in this particular case; but this can be done in a general way, as was pointed out in De Donder's *Gravifigue einsteinienne.*

3. In this third part, "World Geometry," divided into three chapters, Mr. Rice insists first on certain similarities between analytical forms in four variables used in relativity and the forms in two variables used in the differential geometry of surfaces, and shows how the former may be considered as an extension of the latter.

So far the discussion has only concerned the invariant form of the differential equations of physics. But the boundary conditions raise many points of interest, and they have led Einstein to modify his first equations by introducing a "cosmological" term. Two solutions have been obtained, respectively, by Einstein and De Sitter. Both demand a finite three-dimensional universe, but they lead to different views as to the nature of time. The two solutions are completely discussed.

On the other hand, in all the preceding considerations, gravitation has a privileged position as opposed to other physical forces in the relativity theory. Attempts to remove it have been made in successive generalizations by Weyl and by Eddington. But there was still a dissymmetry,

the equations being relative to the ten gravitational potentials and the four electromagnetic potentials. In order to obtain at the same time and in a symmetrical manner both the gravitational and electromagnetic fields, it is necessary to consider potentials in number greater than ten. Einstein accomplished this by suggesting differential equations to be satisfied by the coefficients of parallel displacement or by covariant quantities to Christoffel's symbols.

A characteristic feature is that Mr. Rice presents all the developments in a very simple manner, which may be followed easily. Furthermore, the physical interpretation of the equations plays everywhere an important rôle. This book is highly recommended to students who wish to have a first complete initiation into the relativity theory. It will be a fruitful guide for the further study of the subject.

H. L. VANDERLINDEN

Analyse Spectrale Appliquée aux Recherches de Chimie Minérale. By F. LECOQ DE BOISBAUDRAN AND ARNAUD DE GRAMONT. Paris: J. Herman, 1923. Text and Atlas.

The position which the study of spectra has attained in physical research may lead us to overlook the fact that spectroscopy was originally spectrum analysis, that its early development was largely in the hands of chemists, and that the problem of obtaining quantitative results in the spectroscopic analysis of substances is but partially solved and deserves much further investigation.

The work under review is in part a detailed description of the spectra of certain elements and compounds, with excellent reproductions. This part is by Lecoq de Boisbaudran, who died in 1912, and this section may be regarded as an extension of his early work, *Spectres Lumineux.* The second part is by the late Compte de Gramont, and is a presentation of the methods which made him a recognized authority on the spectrum analysis of minerals. De Gramont's first book on this subject was published in 1895, a time which marked the closing of De Boisbaudran's chief activity, so that in the present publication we have a summary and adaptation to our present needs of the life-work of two men whose investigations along this line extend from 1866 to 1923.

The introduction by De Gramont, entitled "Lecoq de Boisbaudran, sa vie, son œuvre et ses idées," is a highly sympathetic account of the life of an enthusiastic private investigator, working in the new sciences of physical chemistry and spectrum analysis with little to guide him in either, but developing methods and obtaining results of lasting value.

After describing arrangements of the spark suited to the production of spectra from substances in various solid forms and in solution, De Boisbaudran gives tables describing the spectra of over forty substances, spectrograms of which are reproduced in the atlas. These substances are chiefly compounds, some of them of the rare earths and of the metal gallium, of which he was the discoverer. The distinctive feature of these tables is the detailed description of the prominent lines and bands in each spectrum, and the influence upon them of different conditions of discharge. While the charts locate the lines only by micrometric measures, the tables give both these and the value in $\mu\mu$ of each wave-length. In addition to recording De Boisbaudran's later work, this material will be of much assistance to anyone working with the spectra of these substances.

In the second part of the work, written by De Gramont, we have a systematic presentation, prepared especially for chemists, mineralogists, and those working in technical laboratories, of the methods of spectrum analysis developed in his long experience. The treatment is brief and limited in scope, being largely confined, on the instrumental side, to the equipment with which most of his own work was carried out, but the instructions given are those of a master of the technique with which he deals, and De Gramont has been very successful in presenting the methods which he found to give the best results.

Two chapters are devoted to the prism spectroscope and its use with the aid of photography, six types of spectrograph being described, with careful directions as to their most effective use. The diffraction grating is not considered. The following chapters treat of the most useful arrangements of spark according to the form of substance under examination, the use of solutions as spark terminals, and the rapid measurement of the spectrograms for the identification of lines.

The chapter on spectra of dissociation contains a wealth of the author's experience on the use of substances in the solid form, as fused salts or as solutions for the most effective production of their spectra. The devices of the practical spectroscopist for the handling of the air lines and those of the more common impurities are given in detail.

De Gramont's best-known work is his study during many years of the *raies ultimes,* the lines of an element which persist as the quantity of the substance is gradually reduced, studied often to best advantage by means of dilute solutions. These ultimate lines are of use not only in spectrum analysis, but are important in the present frontier work of spectroscopy, as the starting material for the arrangement in series of the many-lined

spectra. The chapter on the ultimate lines is the most complete discussion of them thus far published, and contains a list of these lines with their degrees of sensibility. While De Gramont recognizes that the ultimate lines of an element depend to a certain degree on the manner of excitation, he does not consider the very recent developments of the theory of ionization. It is now quite evident that the ultimate lines of the neutral atom are given in the low-temperature furnace and often in the flame, while in the spark the ultimate lines may be those of the ionized atom. In such a case they are related to the spark spectrum as flame lines are to the arc spectrum.

Quantitative spectrum analysis is becoming a standard operation in industrial laboratories, and the treatment of this method by De Gramont will be found of the highest value. While caution is needed in analysis of this sort, there is no question that much may be accomplished through the observation of the lines which are highly sensitive to the amount of the substance present. A listing of such lines, as selected by the methods of line classification and series grouping, is quite feasible, and will enable much refinement to be introduced into this method of quantitative analysis. As a beginning, the ultimate lines may be used in this way, and the examples of their use by De Gramont, illustrated by the later plates of the atlas, form an excellent guide.

Arthur S. King

Report on Series in Line Spectra. By A. Fowler. Physical Society Publication. London: Fleetway Press, 1922. Pp. 190. 12*s.* 6*d.* net.

Professor Fowler has in this volume put scientific men permanently in his debt. The subject is one to which all who have to do with atoms are turning their attention increasingly, and for a long time it was a painful fact that there existed no book in which the recent results in this intricate subject had been summarized. It is due to the patience and skill of Professor Fowler that this *Report* has already been adopted as a standard reference work, and its appearance has very greatly stimulated the advance of the subject with which it deals.

The *Report* itself is divided into two main sections, the first dealing with a general account of series, and the second including all the numerical data that were available at the time of its publication.

The first part contains nine short chapters, which furnish a clear description of the methods of attack on spectra, the characteristics and relationships of series, the manner in which the frequencies are repre-

sented by formulae, and the success attained in this direction. A chapter is devoted to the work of Hicks, and others to the connections between series and atomic properties, and to the applications of Bohr's theory of atomic structure. Two valuable appendixes give detailed assistance to those who wish to carry out calculations.

The second part of the *Report* is arranged according to groups of chemically related elements, and is a model example of how to present a mass of numerical data so that they will be clear, compact, complete, and readily accessible. The amount of numerical work involved in the preparation of this section must have been very great, and the care with which it has been done is obvious from the rarity even of misprints.

A number of extraordinarily good and well-chosen photographs of spectra are reproduced at the end of the *Report.*

In the present fluid state of this subject, it may almost be said that any book about it will become out of date in the interval between writing and publishing. In this case the inevitable deterioration has been less than might be expected since the book was written by one who is himself in the front rank among investigators in this field. It is a pleasure to be able to add that a new edition is expected to appear shortly, in which the beginnings of the attack upon complex spectra, made possible by the discovery of multiplets, will no doubt be considered, along with other important and very recent advances, many of them due to Professor Fowler himself.

F. A. S.

Seriengesetze der Linienspektra. By F. PASCHEN AND R. GOETZE. Berlin: Julius Springer, 1922. 8vo. Pp. iv+154. M. 11.

Thirteen years ago a doctor's dissertation was published, under Professor Paschen's skilful guidance, by B. Dunz, containing the first summary of what was then known about spectrum series. This little work became during the war one of the rarest and most precious of possessions, for, at the same time that the numbers of workers interested in this field enormously increased, the possibility of obtaining more copies vanished. Soon after the war, Paschen began a revision and, with the help of two of his students, one of whose names shares the title-page, produced the present volume.

In scope the book nearly duplicates the second half of Fowler's *Report on Series in Line Spectra* which preceded it by a few months. Thus it came about that spectroscopists were furnished with two excellent

summaries in this important field, and the long-enduring scarcity is abundantly supplied.

A twenty-page Introduction gives a compact account of series arrangements, including an excellent section on quantum relations, which, together with Zeeman effects and multiplets, are features in which this book excels.

The body of the work treats each element in which series have been found, including all numerical data, with references to the original sources. In a few cases, e.g., *Ne* and *Hg*, illuminating notes are added. The lists are well arranged and seem to be remarkably free from errors. The book ends with useful tables of series terms, and an important page, prepared by Dr. E. Back, showing the Zeeman patterns of series lines, a subject in which the Tübingen laboratory has been pre-eminent.

F. A. S.

NOTICE TO CONTRIBUTORS

There is occasionally published in the *Astrophysical Journal* a Standing Notice (for instance, on pages 179–80 of the number for September 1917). This is principally intended to guide contributors regarding the manuscript, illustrations, and reprints. This notice contains the following paragraph:

> Where unusual expense is involved in the publication of an article, on account of length, tabular matter, or illustrations, arrangements are made whereby the expense is shared by the author or by the institution which he represents, according to a uniform system.

The present sheet has been printed for amplifying further that paragraph.

The "uniform system" according to which "arrangements are made" is as follows: The cost of composition in excess of $50, and of stock, presswork, and binding of pages in excess of 40 pages, for any one article shall be paid by the author or by the institution which he represents at the current rates of the University of Chicago Press. When four articles from one institution or author have appeared in any one volume, on which the cost of composition has amounted to $50 each, or when the total cost of composition incurred by the *Astrophysical Journal* on articles for one institution has reached the sum of $200, the entire cost of the composition, stock, presswork, and binding of any additional articles appearing in that volume shall be paid by the author or by the institution which he represents.

As to illustrations, the arrangement cannot be quite as specific, but it may be generally assumed that not more than three half-tone inserts can be allowed without payment by the author. The cost of paper, presswork, and binding for each full-page insert is about $8.00, aside from the cost of the half-tone itself. In the matter of zinc etchings, considerable latitude has to be allowed, as in many cases diagrams take the place of more expensive tables. It may be assumed, however, that it will seldom be possible for the *Journal* to bear an expense of over $25 for diagrams and text illustrations in any one article.

Contributors should notice that since January, 1917, it has been impossible to supply any free reprints of articles.

Reprints of articles, with or without covers, will be supplied to authors at cost. No reprints can be furnished unless a request for them is received before the *Journal* goes to press.

Every article in the *Astrophysical Journal*, however short, is to be preceded by an abstract prepared by the author and submitted by him with the manuscript. The abstract is intended to serve as an aid to the reader by furnishing an index and brief summary or preliminary survey of the contents of the article; it should also be suitable for reprinting in an abstract journal so as to make a reabstracting of the article unnecessary. For details concerning the preparation of abstracts, see page 231 in the April, 1920, number of the *Journal*.

THE EDITORS